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Biogenic Sulfur Compounds in Coastal Atmospheres of North Carolina

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SECTION I

INTRODUCTION

The existence of "natural" biogenic sulfur contributions to the atmosphere has been recognized for nearly a century (1), but few data have been complied on which to base estimates of the strength of these natural sources or their distribution. Global budgets of atmospheric sulfur estimate the biogenic contributions on the basis of indirect evidence of the sulfur content of rain, rivers, and the atmosphere in remote locations, but the uncertainty of these data and the difficulty of interpreting them yield diverse estimates ranging from about 33 million tons per year (2) to about 100 million tons per year (3,4) in the most recent budgets. These budget estimates must be regarded as very uncertain and of little use for determing the strength of biogenic emissions on a local or even a regional basis.

Interest in the magnitude of these emissions has been heightened by recent reports to the effect that biogenic sulfur sources may make significant contributions to the atmospheric load of particulate sulfate, both in urban and nonurban locations (5,6).

Many biological processes produce volatile sulfur compounds which may be responsible for biogenic sulfur emissions to the atmosphere. These include the bacterially mediated decomposition of organic sulfur present in plant and animal tissue, chiefly in protein, and the respiratory metabolism of the bacterial sulfate reducers. The former process yields a variety of volatile organic sulfur gases and hydrogen sulfide (7,8). The latter produces hydrogen sulfide, which in some circumstances may be transformed either biologically or by means of spontaneous chemical reactions to yield other volatile compounds. Lovelock et al. (9) have proposed that most of the biogenic sulfur released to the atmosphere is dimethyl sulfide derived from the bacterial decomposition process described above. However

extrapolation of these data and recent reports of experimental observations indicate that these processes are unlikely to yield more than a few billion kilograms per year to the global atmosphere (10,11,12).

The total sources of atmospheric S derived from organic S decomposition are limited by the availability of this substance in the standing crop and the proportion that is released as volatile sulfur. Organic sulfur is present only in low concentrations in plant and vegetable matter (0.1 to 1% of the mass of dry organic matter), and the data of Lovelock et al. (9) imply annual release totaling at most only 100 µg/g of organic S present in plant and animal tissue. Even if this release were greatly concentrated in time, the result could not yield an atmospheric concentration exceeding about 1 $\mu g/m^3$ (or about 1 ppb) even in locations where the organic sulfur production of the local biota is extremely high, since the latter rarely exceeds a few grams per square meter per year even in very productive locations. It therefore seems likely that if biogenic sulfur is present in the atmosphere at concentrations exceeding a few ng/m^3 (a few parts per trillion), it must have been produced by sulfate reducers and released either as H_2S, or as DMS or other gases derived from H_2S.

Bacterial sulfate reducers are obligate anaerobes which inhabit aquatic environments where oxygen is absent and sulfate is present in solution together with oxidizable organic matter. The environmentally most important class of sulfate reducers appears to comprise the species Desulfovibrio desulfuricans, but several other species of sulfate reducers exist. It is possible that a recently described bacterium that reduces elemental sulfur to hydrogen sulfide during the respiratory oxidation of acetate may also play an important role in the sulfur cycle of wet sediments (13).

BIOGENIC H_2S IN THE ATMOSPHERE

Direct evidence of H_2S in the natural atmosphere is very scarce, partly because concentrations below about 4 $\mu g/m^3$ (3 ppb) are difficult to measure. Several workers have recently developed techniques for measuring H_2S and/or dimethyl sulfide at concentrations below 1.5 $\mu g/m^3$ (1 ppb) and available evidence implies that tropospheric air sampled at points not near significant anthropogenic or biogenic sulfur sources usually contains less than 0.1 $\mu g/m^3$ (100 ppt) and may have less than 0.01 $\mu g\ m^3$,

(10 ppt). Slatt et al. (17) report that even air that has passed over an estuary, a mangrove swamp, forested parks, residential areas, and/or a sewage plant typically contains less than 1 $\mu g/m^3$ (1 ppb) H_2S. (Their sampling site appeared to be at least 1.5 km from the sewage plant and the nearest mangrove swamp.) These measurements imply either that the lifetime of H_2S in the atmosphere is extremely short or that it is not released to the atmosphere in significant quantities.

It is known that H_2S production by bacterial sulfate reducers may proceed at extremely rapid rates under some conditions. Field studies and laboratory experiments indicate that rates as high as 50 to 400 mg m^{-2} hr^{-1} may be common in suitable habitats (18-23). Relatively little is known about the fate of this H_2S or about the proportion of the sulfide produced in muds that reaches the atmosphere.

Östlund and Alexander (24) present evidence of extremely rapid aqueous oxidation of H_2S by dissolved O_2 in seawater, and conclude that little H_2S produced in submerged marine muds more than a few meters deep can reach the atmosphere, since most of it is oxidized in the water column. They infer that H_2S can be released in significant quantities only from exposed muds of tidal flats or from water only a few meters deep. They estimated the half-life of H_2S in seawater containing O_2 present to excess to be 17 min, but other studies report half-lives in seawater and blackish water ranging from 2 h to more than 100 h, and reports of 12 to 20 h appear to be common (25-29). It follows that exposed tidal flats are likely to be sources of atmospheric H_2S, and that this gas may under some circumstances be evolved from water overlying muds in which H_2S is being produced.

Frequent reports of the odor of H_2S near coastal and inland marshes and swamps, harbors, lakes, tidal mud flats, and irrigated farm land signify that emissions do occur, but few quantitative data are available.

H_2S emission rates for isolated areas have been measured by determining the amount of sulfur released from the surface to a closed chamber placed over the ground or a shallow tidal pool. Using this method, Brannon (30) observed H_2S emission rates ranging from 0.06 to 5.8 mg m^{-2} hr^{-1} in Barataria Bay (Louisiana) Spartina alterniflora marsh soils. He noted that the release

rate varied greatly with the spot sampled, and that H_2S appeared to be escaping preferentially in certain areas through "channelized" escape routes. (Martens 31 has reported a similar phenomenon facilitating the escape of methane from submarine sediments.) Aneja (32) also found that H_2S release rates in the intertidal zone of a S. alterniflora marsh on the coast of Long Island (New York) to be highly variable, ranging from below detection level to 4.7 mg m^{-2} hr^{-1}. He reports that, on some runs, the H_2S concentration inside the chamber exceeded the measurement capability of the gas chromatograph he employed. Hansen et al. (33) employed the chamber method to measure the release of H_2S from shallow-water sediments on a protected shore in Denmark. They found that the observed emission rate from a sandy sediment with a relatively low organic matter content ranged from below the detection limit up to 11 mg m^{-2} hr^{-1} and averaged 2.1 mg m^{-2} hr^{-1}, while that from a small lagoon whose surface sediments contained 20 to 30% organic matter in the form of decomposing eelgrass ranged up to 118 mg m^{-2} hr^{-1} and averaged 53 mg m^{-2} hr^{-1}. The sediments were covered by 1 to 3 cm of water.

The literature contains no measurements of biogenic sulfides in the air near sites where they are produced.

BIOGENIC PARTICULATE SULFUR IN THE MARINE AND COASTAL ATMOSPHERE

If natural sources of sulfur contribute to the atmosphere in marine and coastal locations, then one would expect to find it present in aerosol form in these locations. Aerosol sulfate is a normal constituent of the atmosphere in such locations. Sulfate makes up about 8% of the mass of the principal ions in bulk seawater, and it is injected into the atmosphere together with other seawater constituents by the action of wind and waves. The occurrence of non-sea salt sulfate in the marine aerosol may be demonstrated on the basis of the observed SO_4^{2-}/Na^+ ratio in the aerosol, or on the basis of the size distribution of sulfate-containing particles and their relationship to that of some other conservative tracer of sea salt aerosols. The first method requires the assumption that the process of forming sea salt aerosols does not result in aerosols enriched in sulfate, while the latter requires the assumption that the tracer employed is a conservative one which is neither fractionated in the formation of the

aerosol nor depleted or enriched in the aerosol after it has entered the atmosphere.

In analyzing the composition of aerosols, it is customary to determine the enrichment factor $EF_{sw}(X)$ of the ion or element relative to bulk seawater (34). This may be defined as the ratio of the observed ratio of the element or ion X concentration in the aerosol to a seawater tracer such as Na, to the ratio of the two in bulk seawater:

$$EF_{sw}(X) = (X/Na)_{ob} / (X/Na_{seawater}) \quad (1)$$

If concentration measurements are available, the enrichment may be expressed in terms of the amount by which the abundance of X in aerosol form exceeds the amount that would be present if seawater were the only source, and the ion or element were present together with the seawater tracer in concentrations that match their ratio in bulk seawater:

$$EX_{sw} = X_{ob} - (Na_{ob}(X/Na_{sw})) \quad (2)$$

It will be noted that, when the enrichment factor is less than one, depletion has occurred, and expression (2) will be negative.

Although the marine aerosol has been the subject of intense study for the last decade, there are few reports of the presence of particulate sulfur in marine or coastal locations, and fewer still that include measurements that permit determination of the presence of excess sulfate or an estimate of its abundance. The most interesting studies are those of Buat-Menard et al. (35) and Meinert and Winchester (36). The former measured sodium, chloride, magnesium, potassium, calcium, and the mass of insoluble salts in aerosols collected on shipboard in the open Atlantic Ocean and off the coast of Africa. They observed sulfate enrichment relative to sodium in combination with calcium enrichment and the presence of insoluble salts, which implied that the sulfate was derived from gypsum ($CaSO_4$) in dust advected from the Sahara. Sulfate enrichment was also observed in conjunction with potassium enrichment and chloride depletion in the Gulf of Guinea, and the authors inferred that it was derived as H_2S and/or CH_3SCH_3 from the productive upwelling waters present in the region. The ratio of excess

sulfate to chloride loss implied complete replacement of the chloride anions by sulfate anions.

Meinert and Winchester (36) studied the distribution of Cl, K, S, Fe, and other elements in size-fractionated aerosols collected from marine air on the coast of Bermuda. They observed that all chloride occurred in the largest particles (>2 μm aerodynamic diameter) and determined that it was approximately 20 to 40% depleted relative to K, which was presumed to be of marine origin. In contrast, Martens et al. (37) and Martens and Harriss (38) observed that both Cl and Na of apparent marine origin are present on all stages of an Anderson cascade impactor and also on the after-filters in samples collected in Puerto Rico and at San Francisco Bay. Chloride depletion relative to sodium was observed in most samples and was greatest in the small-particle fraction. In the San Francisco Bay area, the loss of chloride in samples on stages 6 and 7 often exceeded 90%, while losses of 10 to 20% were observed in stages 1 through 4. Total losses averaged for all particle sizes ranged from 6 to 90%. These samples were collected in coastal locations and at sites up to about 30 km from the nearest shore.

Chesselet et al. (39) report an average chloride loss of 4% in aerosols collected over the open ocean. More recently, Gordon et al. (40) present convincing evidence that chloride was not depleted relative to sodium when they sampled aerosols from an aircraft (altitude 75 to 2000 m) on five consecutive days near the Bahamas. The mean ratios of these two elements did not differ significantly from that of bulk seawater throughout the altitude range sampled, though their total concentrations declined from about 4 to 7 $\mu g\ m^{-3}$ at 75 m to about one-tenth that value at 2000 m.

There is evidence that chloride loss, when it occurs, is related to the chemistry of the aerosol and to local gaseous sources of NO_2 or biogenic sulfur. Robbins et al. (41) proposed that HCl is volatilized off the aerosol particle by HNO_3, which results from the uptake of NO_2. Eriksson (42) proposed that chloride loss may be due to uptake of SO_2 followed by its conversion to sulfur trioxide. Martens et al. (37) present evidence supporting the hypothesis of Robbins et al. (41) in the form of correlations between the NO_2 abundance and observed chloride loss in the San Francisco aerosols they studied. They found no correlation between SO_2 and chloride

loss in these samples, but theorized that much of the chloride loss in the Puerto Rican samples (collected in locations where pollutant sources of NO_2 are small) may be due to uptake of SO_2 derived from natural sources in Puerto Rico or in the offshore waters.

The latter explanation is compatible with the results of Junge (43) who found a S/Cl ratio that decreased with increasing particle size, and with those of Meinert and Winchester (36) which show the same kind of relationship. Green (44) reported that the Cl/Na ratio declined with the pH of the aerosol in marine and mixed marine and polluted continental air collected at the coast of southern California. Kadowaki (45) reported the presence of $NaNO_3$ in large particles collected at a seacoast location, and of NH_4NO_3 in small particles, from which he infers that chloride volatilized off large particles by reaction with NO_2.

Taken together, these results imply that biogenic sulfur emissions may lead to the formation of aerosol sulfate, and that this may be reflected in an associated depletion of chloride relative to sodium in sea salt aerosols, which should be most pronounced in the small particle fraction. Chloride depletion in both size fractions may result from the uptake of NO_2, which may also result in the presence of nitrate in the particulate sample. The picture is further complicated by the conclusions of Harker et al. (46) who demonstrate that the nitrate abundance of particulates may be reduced by volatilization of the nitrate (probably as nitric acid vapor) due to interaction with H_2SO_4 produced either locally by photochemical oxidation of SO_2 or contributed as a sulfuric acid aerosol by long distance transport.

We report here the preliminary results of a program of field measurement designed to survey the distribution of hydrogen sulfide, sulfur dioxide, and particulate sulfur, sodium, and chloride in the atmosphere near sites where bacterial sulfate reduction is active. The first study reported here was conducted to determine the sulfide levels present in a tidal marsh and their relationship to the tidal cycle. The second was conducted in an estuarine environment where H_2S-producing muds occurred in bottom sediments but were never exposed to the atmosphere.

SECTION 2

CONCLUSIONS

1. Biogenic sulfur gases were observed in the atmosphere at concentrations ranging up to 80 $\mu g/m^3$ (60 ppb) in a tidal marsh in summer at a site where muds containing high concentrations of biogenic H_2S are regularly exposed by tidal movements, and up to 30 $\mu g/m^3$ (22 ppb) in the fall at three estuarine sites where fine-grained bottom sediments containing H_2S occur one or more meters beneath the surface. In the summer, the biogenic sulfur consisted of H_2S and was found to be highly localized in the atmosphere near the marsh; little was observed at a background site 2.4 km distant from the marsh, even though this site was similar in regard to underwater and exposed sediments to the sites studied in the fall. In the fall, both SO_2 and H_2S of biogenic origin were observed. These two constituents were correlated at one site, which implies that the SO_2 was derived from precursor H_2S. H_2S observed at two other sites 2.5 km apart was correlated, which implies that H_2S had a longer atmospheric lifetime and/or that the sources were widespread. The absence of exposed H_2S-rich muds or of correlation between biogenic sulfur gases in the atmosphere and the tidal cycle implies that the sulfur was evolved from the surface of estuarine water and/or from coarse sand sediments containing relatively little organic matter.

2. This biogenic gaseous sulfur is derived from the metabolism of bacterial sulfate reducers, not from the decomposition of organic sulfur present in plant and animal tissue. This implies that the global and even local sources of significant quantities of atmospheric biogenic sulfur are extremely uneven and that source strengths are highly variable.

3. Biogenic particulate sulfate was observed in the summer at concentrations ranging from about 2 to 13 $\mu g\ m^{-3}$ and averaging about 4 $\mu g\ m^{-3}$ in air masses with marine trajectories; non-sea salt sulfate was observed in

air with mixed continental and marine trajectories at concentrations ranging from 3.2 to 20 $\mu g\ m^{-3}$, and an unknown proportion of this also appears to be biogenic.

4. Chloride loss from sea salt particles, estimated on the basis of the observed sodium concentrations, ranged from 0 to 96% and was strongly correlated with excess sulfate in air samples collected with both marine and mixed marine and continental trajectories in the summer. Chloride loss showed no correlation with excess sulfate, nitrate, ammonium, or excess potassium in the samples collected from air with continental trajectories in the fall.

SECTION 3

METHODOLOGY

HYDROGEN SULFIDE AND SULFUR DIOXIDE

Hydrogen sulfide and sulfur dioxide were collected on treated filters for subsequent analysis by X-ray fluorescence spectroscopy. Millipore WSWP04700 filters (47 mm o.d) were mounted in a modified Millipore single filter holder No. XX-50-04700 which was elongated so that it could hold three filters in series, separated with stainless steel rings fitted with Teflon or Viton rings to seal the filter elements in the holders. Air is drawn through the filter holder by a vacuum pump, the flow rate being controlled by a critical orifice attached to the outlet of the filter holder.

The first filter in the series (the prefilter) was untreated and was used to remove particulate matter from the sampled air. The second filter was treated with a LiOH solution to collect SO_2, and the third with $AgNO_3$ to collect H_2S. After use, the filters were returned to the laboratory and analyzed for sulfur content by energy dispersive X-ray fluorescence to determine the abundance of S on the surface of each filter (47). This method of analyzing for sulfur determines the mean S abundance cm^{-2} by a procedure which in effect "weighs" the result in favor of the abundance present in the center of the filter, hence it tends to give erroneous results if the collected sample is not evenly deposited over the treated filters.

Several potential sources of measurement error in this collection system were evaluated in the laboratory: (a) absorption of sulfur gases on the prefilter; (b) inefficiencies in the collection of SO_2 or H_2S by the treated filters; (c) penetration of the collected gas into the treated filter, so that it cannot be detected by the X-ray fluorescence technique; (d) interference through collection of H_2S or other sulfur gases by the

LiOH filter, or of SO_2 that has passed through the first filter or other reactive gases by the $AgNO_3$ filter; (e) losses of the collected gas after exposure in the field, or migration of the sulfur into the filter where it cannot be detected; and (f) inhomogeneous deposition of the sample on the treated filters.

These error sources were evaluated in the laboratory by a series of tests in which an air stream containing gas of known concentration was passed through the filters, separately or in combination, with and without a prefilter. Sulfur gas concentrations were measured in the air stream ahead of and behind the filters, and the concentrations collected on the filters were measured by X-ray fluorescence. Tests were conducted in a variety of combinations of flow rate, relative humidity, exposure duration, temperature, etc. The efficiency of the collection system was determined by comparing the observed results with what should have been observed assuming 100% efficiency of collection and even deposition on the surface of the filter.

These tests demonstrated that the apparent collection efficiency of the LiOH filters varies with flow rate and relative humidity, and that the optimum flow rate for SO_2 collection by the LiOH filters is 1.0 min^{-1}. At this rate the collection efficiency averages 89% for relative humidities in the range 30 to 90%, while collection efficiency declines to 77% at a relative humidity of 100%.

The collection efficiency of the $AgNO_3$ filters for H_2S was found to be lower and more variable than that of the LiOH filters for SO_2. The average observed for flow rates in the range 0.5 to 2 l min^{-1} and relative humidities in the range 10 to 90% was 78 ± 18%. At 1.0 l min^{-1} the mean observed collection efficiency was 81 ± 3%, while at 2.0 l min^{-1} it was 78 ± 4%. Temperature variations characteristic of ambient air had little effect on these collection efficiencies.

Both filters were found to have good selectivity for their respective gases when freshly made, and the LiOH retained good selectivity for a month after preparation. However, the $AgNO_3$ filters began to collect small quantities of SO_2 after approximately 2 days. For this reason, the

LiOH filter was placed ahead of the $AgNO_3$ filter in the holders when used in the field.

The collection efficiency of the $AgNO_3$ filter for dimethyl sulfide was tested, and no uptake was detected. Shelf life tests indicated that the collected SO_2 is stable on the filter for longer than 2 weeks, but that the measured S concentration on the $AgNO_3$ filters exposed to H_2S begins to decline after about 1 week of storage and may reach 50% or less in a month. The factors influencing this decline have not been examined.

These tests indicate that in field use, the SO_2 measurements obtained with the LiOH filters will underestimate the amount present in the sampled air by about 10%, while the H_2S measurements obtained with the $AgNO_3$ filters will underestimate the amount by about 20%.

Detection thresholds for each gas depend on the flow rate, the duration of sample collection (exposure) and the sensitivity of the X-ray fluorescence measurements, which was 0.05 μg S cm^{-2}. Detection thresholds for the various exposure times and flow rates used in the two studies are shown in Table 1, calculated under the assumption of 100% collection efficiency and the most likely efficiencies obtained in the field (85% for SO_2 and 84% for H_2S at 1.0 l min^{-1} and 80% for H_2S at 2.0 l min^{-1}).

PARTICULATE SAMPLES

Particulates were collected in standard Hi-Vol samplers equipped with flow rate controllers to insure constant flow rates. Pallflex TX40120WW filters were employed because of their inherent low blank values for S, and because they do not significantly collect SO_2 from ambient air.

SO_4^{--}, Cl^- and NO_3^- were determined by the ionic chromatographic technique using a water extract of half of the filter. This extract was also used to determine NH_4^+ by the ion selective electrode technique, and the Na and K by atomic absorption. An acid leach of one quarter of each filter was used to determine Fe, Ca, Pb, and V by atomic absorption. The graphite furnace technique was used to determine V, and the conventional flame technique was used for the determination of Fe, Ca, and Pb.

TABLE I. DETECTION LIMITS FOR SO_2 AND H_2S

Sampling time (hours)	Flow rate (liters min^{-1})		Theoretical limit* $\mu g/m^{-3}$	ppb	Most Proabably limit+ $\mu g/m^{-3}$	ppb
4	1	SO_2	3.7	1.4	4.5	1.7
		H_2S	2.0	1.4	2.4	1.7
6	1	SO_2	0.9	2.4	2.7	1.0
		H_2S	0.9	1.3	1.4	1.0
	2	H_2S	0.5	0.7	0.9	0.6

*Assumes 100% collection efficiency, and a detection level of 0.05 $\mu g\ cm^{-2}$ of filter.

+Assumes average collection efficiencies of 89% for SO_2 and 81% for H_2S at 1.0 l min^{-1} and 78% at 2.0 l min^{-1}.

Table 2 shows the mean blank levels observed during the Morehead City studies reported below together with the detection limits of the techniques employed, expressed in mg per filter, and in $\mu g\ m^{-3}$, calculated on the basis of the average sample volume (1800 m^3). The blank levels observed in the second series of studies at Swansboro were very similar. Ca blank levels were too high to make useful measurements of this element possible.

Total suspended particulate loadings were determined gravimetrically for the second series of studies at Swansboro, but the filter weighings prior to the first series were found to be insufficiently accurate to permit accurate estimates of TSP values, because the mass loading turned out to be very low.

TABLE 2. HI-VOL FILTER MEAN BLANK LEVELS AND DETECTION LIMITS OF PARTICULATE ANALYSIS TECHNIQUES

Constituent	Mean blank level (mg filter^{-1})	Mean blank level ($\mu g\ m^{-3}$)	Detection limit (mg filter^{-1})	Detection limit ($\mu g\ m^{-3}$)
SO_4^{--}	0.98	0.54	0.1	0.06
Cl^-	0.24	0.13	0.02	0.07
NH_4^+	<0.03	<0.017	0.03	0.017
NO_3^-	0.14	0.08	0.04	0.002
Na	2.73	1.52	0.004	0.002
K	0.33	0.18	0.008	0.004
Ca	7.4	4.1	0.003	0.002
Fe	0.16	0.089	0.005	0.003
Pb	0.04	0.022	0.02	0.011
V	<0.003	<0.002	0.003	0.002

SECTION 4

SITE DESCRIPTIONS AND EXPERIMENTAL PROTOCOLS

SITE DESCRIPTIONS

The two sites chosen for this study are located on the coast of North Carolina, one in Morehead City, and one approximately 30 km west near the small village of Swansboro (Figure 1). The Atlantic coast from New England to Florida has a series of narrow offshore barrier islands, which result in the creation of protected sounds between the islands and the mainland coast. These sounds and the mouths of rivers and creeks flowing into them make up a series of shallow estuaries which are flushed to varying degrees by the tides. On the North Carolina coast, the bottom sediments of sounds and estuaries are relatively coarse grained compared to those found north of Delaware Bay or to the south on the shores of South Carolina and Georgia. On this coast, tidal volume is low compared to the area of the sounds and estuaries behind the barrier islands; consequently, tidal excursions are minimal, and the area of tidal mud flats is negligible in most locations. These sites were chosen because of (a) their convenience to Raleigh-Durham, North Carolina; (b) the presence of access roads, docks, sources of power, and other amenities; and (c) the absence of sites of significant sources of anthropogenic SO_2 or other common atmospheric pollutants.

The surrounding countryside is forested, and much of it is swamp land, part of the Great Dismal Swamp of Virginia and North Carolina. This is a freshwater, peat-forming system with relatively low sulfate levels (less than 10 mg/liter and low pH, which we judged to have relatively little capacity for the production of H_2S by sulfate reduction on account of its similarity to other freshwater peat-forming swamps on this coast (48).

Morehead City is a port town with a population of 5300 whose major industry is summer tourism and several military bases located in the vicinity.

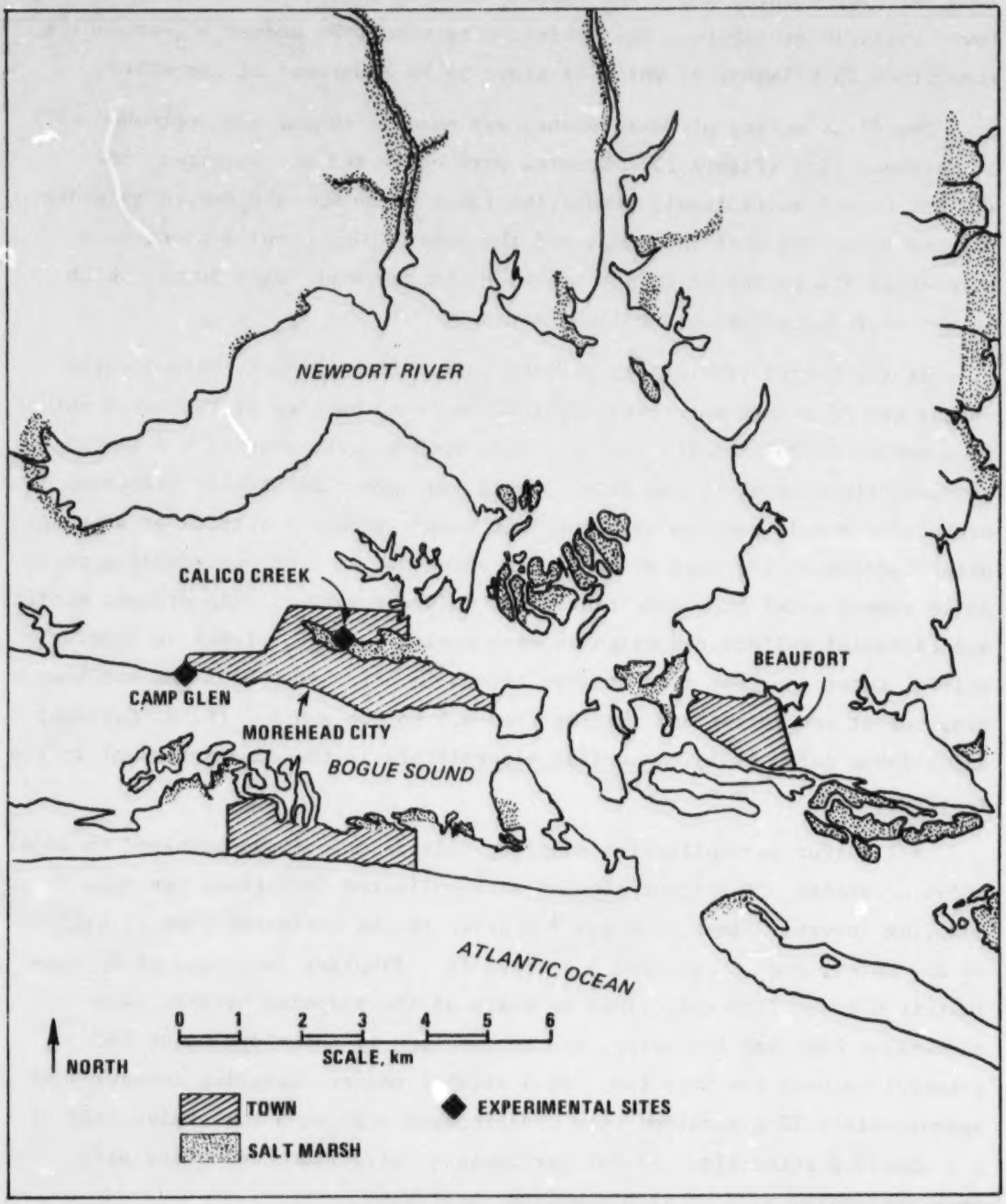

Figure 1. Morehead City sites.

There are few anthropogenic SO_2 sources here or in adjacent Beaufort, and fewer still in Swansboro. The nearest city with even modest SO_2-producing industries is Wilmington, which is about 85 km southwest of Swansboro.

The first series of measurements was made in August and September 1976 in Morehead City (Figure 1). Samples were collected at two sites, one (Calico Creek) an extremely productive tidal marsh where H_2S-rich muds are exposed twice daily at low tide, and the other (Camp Glen) a background site about 2.4 km ESE of Calico Creek on the shore of Bogue Sound, which is not near any organic-rich tidal marshes.

At the Calico Creek site, gas and particulate samplers were located on the end of a dock extending about 100 m from the edge of the marsh out to a narrow channel in its center. Muds were exposed about 2 m below the gas collectors at every low tide. These muds are biologically extremely productive due in part to high nutrient supply from the outflow of a sewage plant located at the head of the creek about 0.6 km from our sampling site. As is common under such conditions, the muds are very rich in organic matter, and bacterial sulfate reduction is very active. The H_2S level in interstitial water in these muds at this season is often very high and has been measured at concentrations ranging from 0.5 to 3.6 m M l^{-1} (P. R. Carlson, unpublished data, 1976). Spartina alterniflora is the dominant plant in the marsh.

All sulfur gas collection sampling intervals were synchronized to local tidal movements. Four-hour samples were collected four times per day, the sampling interval timed to begin 2 h prior to the estimated time of high or low water, and to continue 2 h after it. Sampling intervals of approximately 6 h duration were timed to begin at the midpoint between each successive high and low water, and to continue to the midpoint of the interval between the next two. In a similar manner, sampling intervals of approximately 12 h duration were synchronized with each successive pair of 6 h sampling intervals. Hi-Vol particulate collections coincided with each successive pair of 12 h sampling intervals.

Wind speed and direction were recorded by means of a portable meteorological tower also located on the end of the dock.

Gas and Hi-Vol samples were collected at the background site on the roof of a two-sotry building approximately 12 m above ground level, and 50 m north of the shore of Bogue Sound. This building is approximately 100 m south of a moderately well-traveled highway (U.S. 70) and 250 m south of a hospital, both of which probably constitute modest sources of antoropogenic SO_2. Gas sampling intervals of 6- and 12-h and Hi-Vol sampling intervals were synchronized with local tide movements in the sound in the manner described above for Calico Creek. The tidal movements in the sound at this point are about 1 h ahead of those in the marsh at Calico Creek. There are no tidal marshes in the near vicinity of the Camp Glen site, although anoxic sediments occur offshore in the sound (49, 50). The nearest tidal marshes are across the sound at least 1 km distant, but these are neither extensive nor biologically very productive compared to those at Calico Creek.

Wind speed and direction data for this site were supplied by the University of North Carolina Marine Sciences Institute, which occupies an adjacent building.

ESTUARINE EXPERIMENT

The estuarine experiment was conducted at three sites approximately 35 km west of Morehead City near the small village of Swansboro at the mouth of the White Oak River (Figures 2 and 3). This site was selected because there are few local sources of anthropogenic sulfur. The surrounding land is forested, with no farms and few occupied residences within 10 km.

One of the collection sites was located at the Swansboro Coast Guard Station on the western tip of Bogue Banks on the shore of the sound about 300 m east of the inlet, where large volumes of water are exchanged four times per day through Bogue Inlet between the Atlantic Ocean and Bogue Sound and other estuaries (Figure 2). These exchanges result in a highly variable current flow, which is quite swift at times. There are a number of sand bars in the near vicinity, which are exposed by tidal movements, and some marshes with relatively coarse-grained sediments within 1 to 3 km of this sampling site (Figure 3). Gas collectors operated at 1 l min^{-1} were positioned within 2 m of the water's edge (high tide), and 6-h H_2S and SO_2

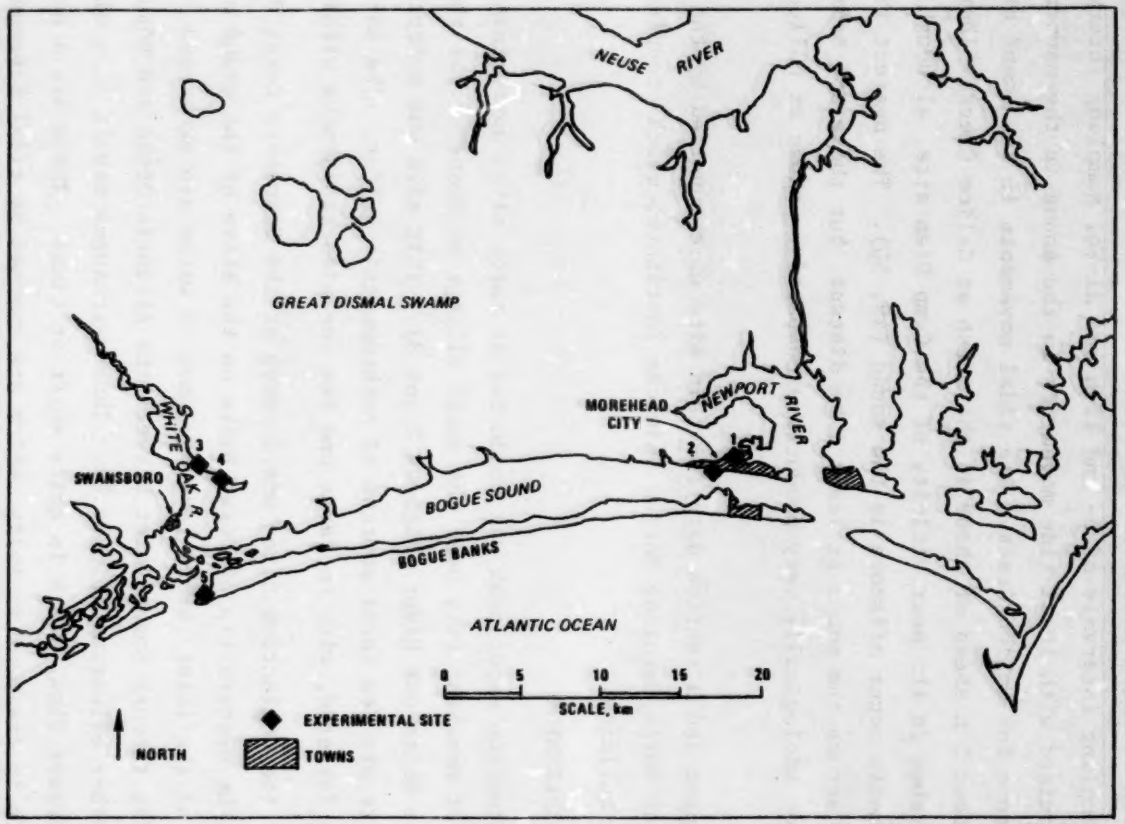

Figure 2. Swansboro and Morehead City. Locations marked 1 and 2 are Morehead City sites; 3,4, and 5 are Swansboro sites. The Great Dismal Swamp is a freshwater swamp.

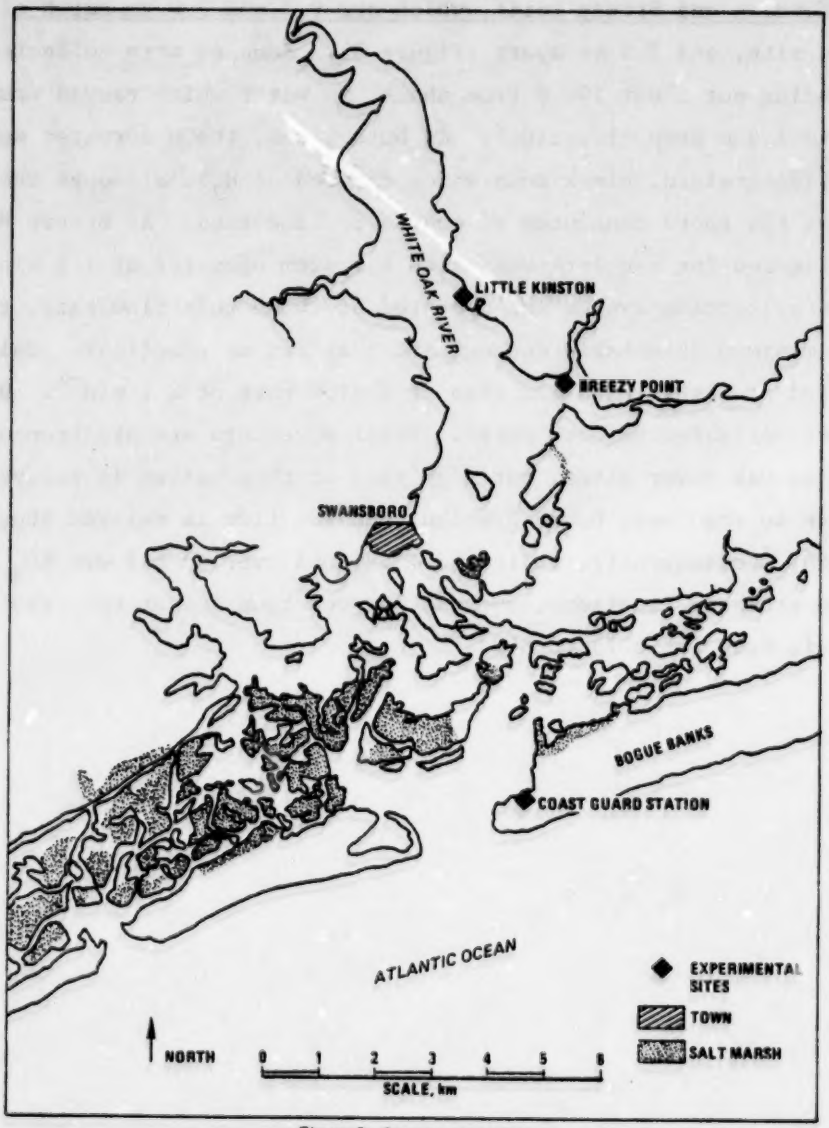

Figure 3. Swansboro sites.

collection intervals were synchronized with the local tide movements in the manner described above. Hi-Vol sample collection intervals of four complete tidal cycles (about 25-h duration) were made daily.

The two other collection sites were located on the White Oak River at Little Kinston and Breezy Point, which are 9.2 and 7.0 km north of the Coast Guard site, and 2.5 km apart (Figure 3). Samples were collected from docks extending out about 100 m from shore, in water which ranged from about 1.0 to 1.5 m deep (low tide). At both sites, the underwater sediments were very fine-grained, black muds which smelled of H_2S, although the sediments at the shore consisted of coarse to fine sand. At Breezy Point, SO_2 was collected for 6-h intervals with a system operated at 1 l min^{-1}, but the H_2S collection system was operated at twice this flow rate, to reduce the minimum detectable concentration as far as practical. Only H_2S was collected at Little Kinston, also at a flow rate of 2 l min^{-1}. Hi-Vol samples were collected at both sites. Tidal movements are synchronous at the two White Oak River sites, but high tide at these sites is delayed about 1 h relative to the Coast Guard Station, and low tide is delayed about 1 h and 45 min. Consequently, while there is 100% overlap between SO_2 and H_2S samples at these locations, overlap between them and at the Coast Guard site is only about 75 to 80%.

SECTION 5

RESULTS

HYDROGEN SULFIDE AND SULFUR DIOXIDE

Morehead City

Hydrogen sulfide was observed in the air about the exposed muds at Calico Creek at every low tide, and comparison of 4-, 6-, and 12-h measurements showed that the average H_2S concentrations appeared to vary systematically with the amount of mud exposed (Figure 4). We infer, therefore, that the peak concentrations corresponding to the lowest water levels were much higher than the 4-h means reported here. Since sulfide was detected at low tide on every 4-h filter, we will confine our attention to the measurements obtained with these filters. The measurements reported assume 100% collection efficiency and hence probably underestimate the H_2S concentrations in the sampled air.

In contrast with the high sulfide levels observed in the marsh, the measurements made at the Camp Glen background site indicated that H_2S almost never exceeded the detection threshold 1.6 $\mu g/m^3$ (1.1 ppb) there. Sulfur dioxide was rarely detected at either site.

The results of this study are summarized in Table 3, where mean H_2S and SO_2 concentrations are calculated from the measurements that exceeded the detection limit, and the number of observations where the detection limit was not exceeded is also shown. At Calico Creek, hydrogen sulfide exceeded the detection threshold at high tide only three times, when the measured concentrations ranged from 2.0 to 2.7 $\mu g/m^3$ (1.4 to 1.9 ppb). In contrast, the 4-h mean H_2S observations at low tide ranged from 3 to 80 $\mu g/m^3$, (1.9 to 56.6 ppb). Sulfur dioxide exceeded the detection limit on only 8 of the 52 observation periods and ranged from 3.7 to 5.6 $\mu m/m^3$, (1.4 to 2.1 ppb). The average low tide H_2S concentration was 15.3 ±

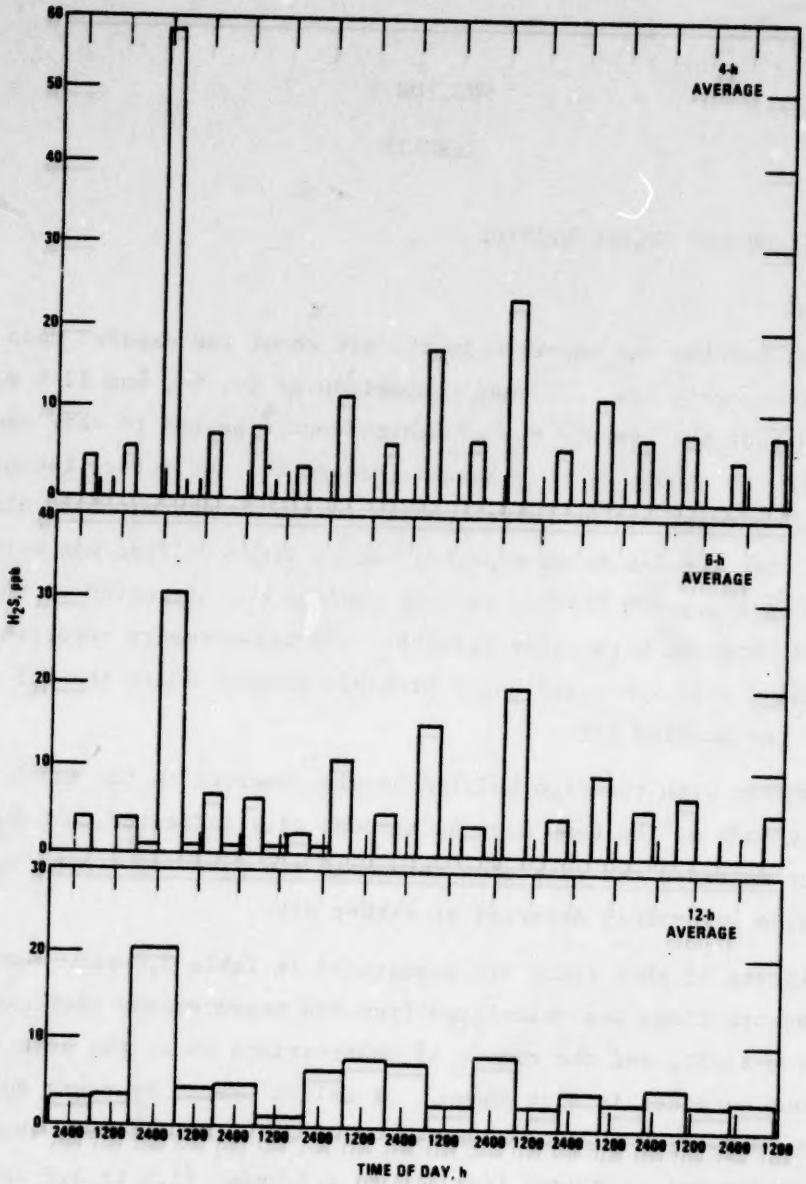

Figure 4. Comparison of 4-, 6-, and 12-h mean H_2S levels at Calico Creek marsh.

TABLE 3. MOREHEAD CITY H_2 AND SO_2*

A. Calico Creek (4-h filter)

	H_2S Mean	H_2S <Det. Lim.	SO_2 Mean	SO_2 <Det. Lim.
Low Tide				
Night	14.4±7.0 (16)	---	1.4±1.5 (2)	14
Day	5.0±1.2 (10)	---	1.5±0.1 (3)	7
All points	10.8±7.6 (26)	---	1.4±0.5 (5)	21
High Tide				
Night	1.7±0.5 (2)	14	---	16
Day	1.4 (1)	9	1.5±0.1 (3)	7
All points	1.6±0.3 (3)	23	1.5±0.1 (3)	23

B. Calico Creek (4-h filter)

High Tide		
Calm	1.9 (1)	6
280° to 20°	---	4
Other directions	1.6±0.3 (3)	12

C. Camp Glen (roof) (6-h filter)

	H_2S Mean	H_2S <Det. Lim.	SO_2 Mean	SO_2 <Det. Lim.
Low Tide				
Night	1.0 (3)	14	1.3±0.5 (5)	10
Day	---	11	1.0 (1)	10
All points	1.0 (3)	25	1.3±0.4 (6)	20
High Tide				
Night	1.0 (1)	16	---	17
Day	---	10	1.1±0.2 (4)	6
All points	1.0 (1)	26	1.1±0.2 (4)	23

*Arithmetic mean in ppb ±2 standard errors of the mean. N shown in parenthesis. Column two shows the number of observations lower than the detection limit. Means calculated from values exceeding detection threshold.

6.5 $\mu g/m^3$ (10.8 ± 4.6 ppb). Hydrogen sulfide concentrations were found to be highest at night, when air movement was limited. At night, the measured 4-h mean concentrations ranged from 4 to 8.0 $\mu g/m^3$ (2.8 to 56.6 ppb) and averaged 20.5 ± 9.9 $\mu g/m^3$ (14.4 ± 7 ppb). Windspeeds averaged 1.8 m s^{-1} at night. In the daytime, the low tide H_2S 4-h concentrations ranged from 2.7 to 10.7 $\mu g/m^3$ (1.9 to 7.5 ppb) and averaged 7.1 ± 1.7 $\mu g/m^3$ (5 ± 1.2 ppb) while the windspeed averaged 5.5 m s^{-1} (Figure 5). Analysis of the dependence of low tide hydrogen sulfide level on windspeed showed that the concentrations declined exponentially with increases in windspeed, the coefficient of correlation of hydrogen sulfide mean with log windspeed being -0.73, which is significant beyond the 0.01 level (Figure 6). In contrast, no significant relationship existed between daytime low tide hydrogen sulfide levels and windspeed. We found no relationship between SO_2 and the tidal cycle, windspeed, or local H_2S level.

Sewage plants can be significant sources of atmospheric H_2S and other sulfur gases; consequently, it is possible that the nearby sewage plant contributed some contaminants to our observations. We evaluated this possibility by comparing samples collected under air movement conditions that would promote such contamination with those collected under other conditions. We assumed that if such contamination occurs, it would be most evident either when there was little air movement (which would promote the accumulation of sewage emissions in local surface air), or when the wind blew directly from the sewage plant to the collection site. Since the depth of the water in the estuary does not influence the atmospheric release of sewage effluents (the outflow pipe being below the low tide level), it is clear that sewage plant contamination can be determined by comparing the hydrogen sulfide levels observed at high tide during conditions promoting contamination with those observed at high tide under other conditions.

The 27 high tide observations were found to be distributed as follows: 4 occurred when the wind direction favored contamination (mean wind direction within ± 50° of the direction of the sewage plant for one or more hours), and 7 occurred under calm conditions (mean hourly wind speed less than 0.45

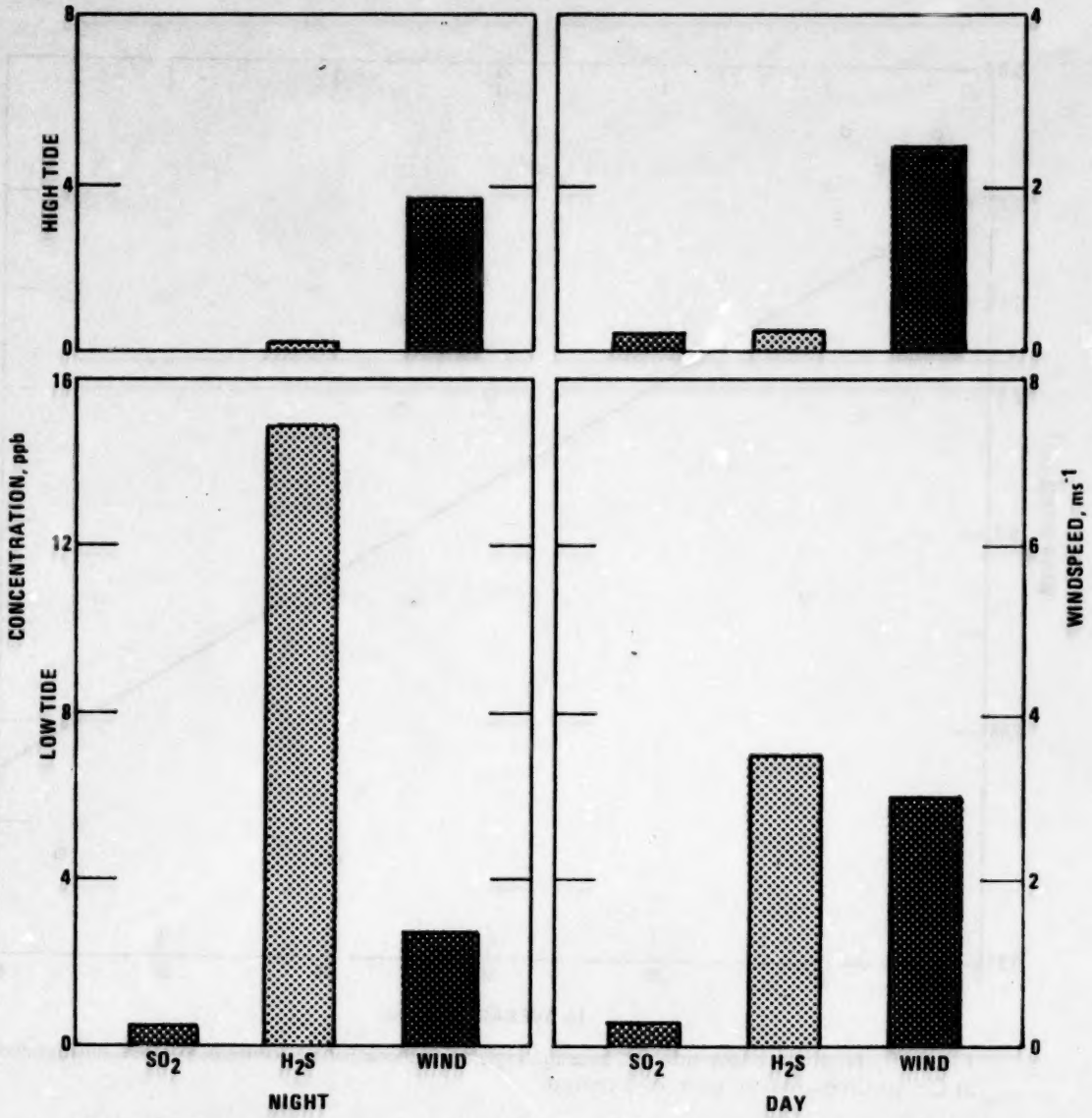

Figure 5. Means of 4-h average H_2S and SO_2 concentrations and windspeed at Calico Creek marsh.

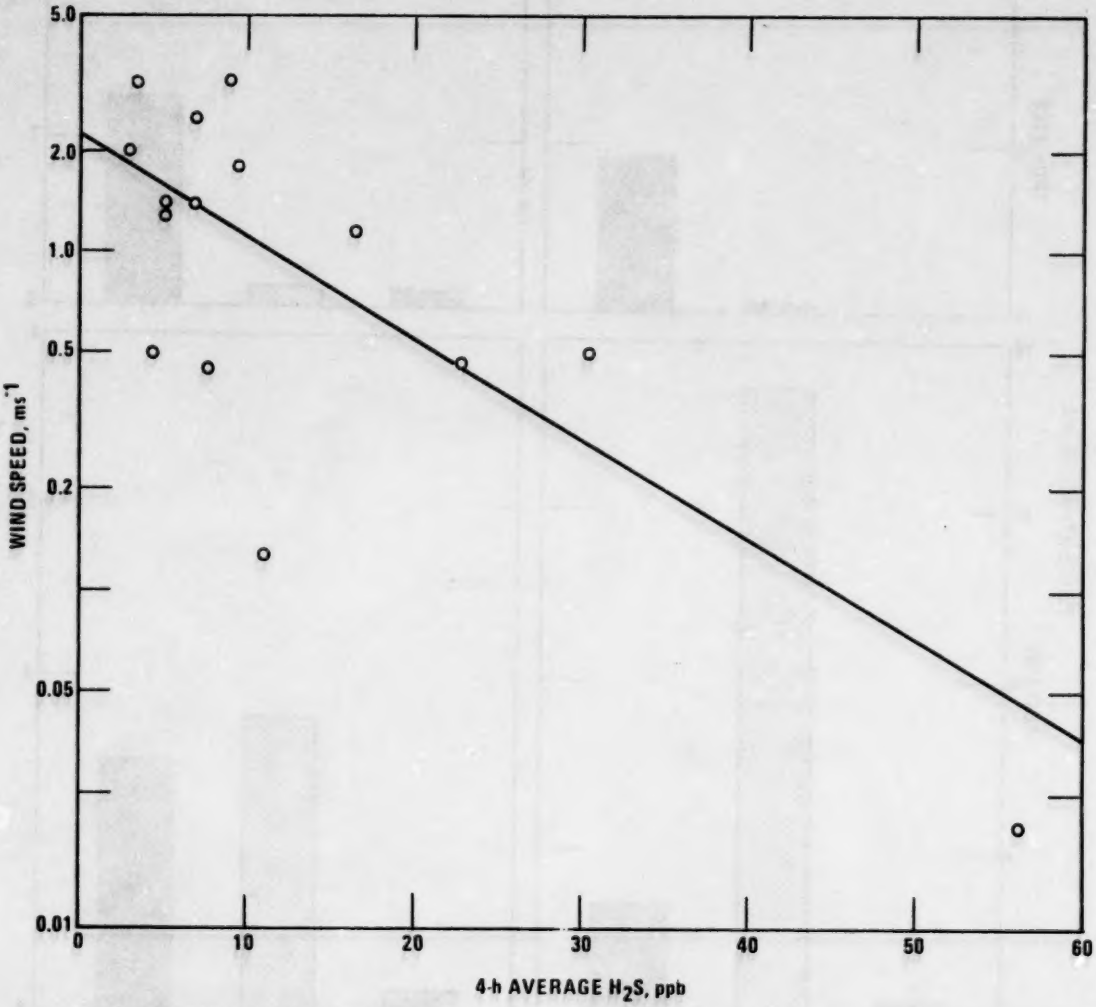

Figure 6. Nighttime low tide 4-h average H_2S concentrations and mean surface windspeed at Calico Creek marsh, over 15-d period.

m s^{-1} for one or more hours). The concentrations observed at these times are summarized in Table 3. H_2S exceeded the detection limit during only one of these 11 intervals, at which time it averaged 2.7 $\mu g/m^3$ (1.9 ppb). In contrast, during the remaining 15 high tide intervals, H_2S exceeded the detection limit only twice, averaging 2.0 $\mu g/m^3$ (1.4 ppb) both times. These observations support the conclusion that there was no sulfide contamination from the sewage plant.

The results observed at the Camp Glen roof are shown in Table 3. H_2S was detected only twice, and never exceeded 2.8 $\mu g/m^3$ (1 ppb). SO_2 was detected in the range 2.4 to 6.1 $\mu g/m^3$ (0.9 to 2.3 ppb) only 9 times out of the total of 53 observation intervals and was observed equally often at low tide and at high tide, night and day. At these times the SO_2 levels exhibited no significant relationships to windspeed or wind direction, or to the levels observed nearly simultaneously in Calico Creek, only 2.4 km distant. On the night on which the H_2S reached 80 $\mu g/m^3$ (56.6 ppb) during the 4-h period of lowest water in Calico Creek, it averaged only 2.0 $\mu g/m^3$ (1.4 ppb) at the Camp Glen roof site during the 6-h interval beginning about 2 h before the corresponding Calico Creek sample and ending almost simultaneously with it.

Swansboro

Adverse weather conditions and power outages greatly restricted the number of useful observations from this experiment, so that only about 14 6-h samples were ultimately available for each site. However, the results were extremely interesting in that they contrasted surprisingly with those obtained in the marsh earlier in the year (Table 4). We found the H_2S was detectable at all sites most of the time, while sulfur dioxide was present in measurable concentrations during all but two sampling intervals. H_2S ranged up to nearly 7.0 $\mu g/m^3$ (5 ppb) at the estuarine sites, and from about 1.4 to 3.7 $\mu g/m^3$ (1 to 2.6 ppb) at the Coast Guard Station. SO_2 ranged up to 42.6 to 45.2 $\mu g/m^3$ (16 to 17 ppb) at both locations where it was measured.

We observed no systematic differences in mean H_2S or SO_2 concentrations with tide at any site, and no significant differences between mean H_2S and

TABLE 4. SWANSBORO H_2S AND SO_2 RESULTS*

		Mean H_2S	Mean SO_2
A.	Breezy Point		
	Low Tide	1.8±1.0 (6)	3.8±2.6 (5)
	High tide	2.0±0.8 (8)	4.5±5.6 (5)
	All points	1.9±0.4 (14)	4.1±3.0 (10)
B.	Little Kinston		
	Low tide	1.3±0.4 (5)	---
	High tide	2.1±1.4 (5)	---
	All points	1.7±0.8 (10)	---
C.	Coast Guard Station		
	Low tide	1.5±0.8 (8)	5.4±4.0 (7)
	High tide	1.6±0.5 (6)	5.8±6.2 (5)
	All points	1.5±0.3 (14)	5.6±3.4 (12)

*Arithmetic mean in ppb ± 2 standard errors of the mean. N shown in parenthesis. Means calculated from values exceeding detection threshold.

SO_2 values at any site. However, comparison of the H_2S levels observed during simultaneous collection intervals revealed a systematic tendency for slightly higher levels to be recorded at Breezy Point than at Little Kinston, and this tendency was found to be significant beyond the 0.01 level as determined by the Sign Test (51). SO_2 values observed at the Coast Guard site and at Breezy Point were examined for any tendency to correlate, but none was found. In contrast, H_2S at Breezy Point was found to correlate significantly with H_2S at Little Kinston ($r = 0.61$, which is significant beyond the 0.05 level). SO_2 and H_2S values measured at the Coast Guard Station were positively correlated ($r = 0.60$, which is significant beyond the 0.005 level), but no evidence of such a correlation was observed at Breezy Point. Analyses of the relationship between windspeed and SO_2 or H_2S levels showed no correlation at any location, but the total number of sampling periods was far too small to enable us to distinguish any interaction among tide, diurnal cycle, and windspeed that may have been present.

PARTICULATE ABUNDANCES AT MOREHEAD CITY

Data Analysis Methods

The observed sodium concentrations in each sample were used to estimate the total sea salt contributions of sulfate, chloride, and potassium on the basis of their abundance relative to sodium in bulk seawater:

$$Cl/Na_{sw} = 1.79$$

$$SO_4/Na_{sw} = 0.25$$

$$K/Na_{sw} = 0.037.$$

Excess sulfate, chloride, and potassium were calculated for these constituents, together with the corresponding enrichment factors. Air mass trajectory analyses were employed to classify samples according to the apparent origin and history of the air mass sampled.

Differences in the sample characteristics as a function of site and air mass origin were investigated by several techniques. Since particulate abundances and enrichment factors tend in general to be lognormally

distributed, estimates of central tendency and judgments of the statistical validity of differences between mean abundances, correlation coefficients, and so forth require that the original data points be converted to their logarithms. Therefore, comparisons of the differences in mean abundances were based on the means of the logs of the individual observations. In addition, some nonparametric tests of the significance of the difference between the abundances of paired roof/marsh samples were used. These were the Sign Test and Wilcoxson's Signed Rank Test (51).

Physically realistic models of the relationships between particulate components suggest that they should be linearly related. This is especially true regarding the possible causes of element or ion enrichment in the formation of sea salt particles, anion replacement, and the relationship between the abundances of constituents of interest collected at the two different sites. Consequently, we explored these phenomena by linear regression analyses, recognizing that it is, strictly speaking, meaningless to speak of the statistical significance of the resulting correlations or of the values of the slope and intercept of the resulting regression lines. In discussing these, no reference is made to their possible statistical validity.

Air Mass Origins

Sampling days were classified as "marine" or "mixed marine and continental" on the basis of 96-h backwards trajectories calculated by the method of Heffter and Taylor (52) at 6-h intervals. If all trajectories showed at least 72 hours over the ocean and no time over land, the day was classified as "marine", but if the time over the ocean were shorter, or the trajectory began on the continent, passed over the ocean, and then returned to the coast at our site, it was classified as "mixed marine or continental". Of the total 14 sampling intervals, 7 were classified as "marine" and the remainder "mixed marine and continental". One of the latter was purely continental, three corresponded to days when the air mass left the coast and spent 12 to 60 hours at sea before returning to land, and the remaining three had wholly marine trajectories, but were only 36 to 72 hours long (lack of reporting weather ships making longer trajectories impossible to calculate).

We observed no consistent relationships between trace metal abundances and air mass origin, but this is not surprising in view of the possibility that local sources of both fugitive dust and automobile lead pollution could lead to variable concentrations of iron and lead independently of the trajectory of the air mass. Vanadium concentrations on "marine" days were below the detection level (2 ng m^{-3}) in 3 of the 14 samples, and averaged 3.4 ng m^{-3} in the remaining. This is high compared to marine air (0.2 to 0.4 ng m^{-3}), but compares well to concentrations in very remote continental regions at some isolated shore locations (1 to 3 ng m^{-3}) (34). Vanadium concentrations were somewhat high on "mixed" days, when they averaged nearly 6 ng m^{-3} in the 12 samples with values above the detection threshold.

INFLUENCE OF AIR MASS TRAJECTORIES AND COLLECTION SITE ON SAMPLE COMPOSITION

The analyses of these data may be approached in two ways. One is to group together both air mass trajectory classes, on the grounds that differences between them will probably be slight and difficult to interpret, in view of the fact that all samples appear to contain a significant marine component, and the effects of continental contributions collected before the air mass arrived at our site cannot be readily distinguished from "continental" contributions of local origin. The other way is to analyse each of the two types of samples separately and look for characteristics that are consistent within air mass trajectory classes, and not present when the classes are combined. We have conducted both kinds of analyses.

The marine influence inferred from the air mass trajectories was apparent in the presence of sodium in all samples. It ranged from about 1 to 4 μg m^{-3}. Excess sulfate was present in all, in concentrations ranging from about 1.5 to over 20 μg m^{-3}, and chloride enrichment factors ranged 1.0 down to 0.04. Sea salt concentrations ranged from about 2 to 8 μg m^{-3} and appeared to be slightly higher in samples from "mixed" air mass trajectories, although the differences were not statistically significant.

Sulfate, chloride, sodium, and potassium concentrations at the two sites were very similar on all sampling days except the last, when a high sulfate concentration at the roof site combined with other anomalies to suggest contamination of this sample. Consequently, we have not included it in the results reported here.

Geometric mean concentrations of all constituents of interest and of enrichment factors are shown in Table 5. Statistical comparisons of the means revealed no significant differences between sites or between types of days at either site. Analyses of the differences between concentrations in the roof site sample and the marsh sample on corresponding days by means of the Sign Test showed that when all 13 pairs of measurements are considered, chloride, nitrate, sulfate, and excess sulfate are significantly more abundant at the roof site than at the marsh. This is not true of sodium or excess chloride.

The presence of excess sulfate in all samples implies that it is derived at least in part from natural marine sources of biogenic sulfur, but it is not possible to determine whether these sources are local or are contributed from the open ocean. Previous workers have shown that chloride loss in marine aerosols may be due to absorption of gaseous biogenic sulfur, and that the presence of biogenic sulfate in the aerosol may be associated with excess potassium. Buat-Menard et al. (35) found both in aerosols collected near upwelling regions in the Atlantic Ocean and speculated that the potassium was derived from the film of surface organic matter, while the sulfate was derived from biogenic sulfides that evolved from the water. Therefore, it is instructive to examine the relationships among excess sulfate, excess chloride, and excess potassium in our samples to see whether it is possible to observe an effect local to one of the two sites, which may implicate local sources of biogenic sulfur or other important constituents.

Systematic differences at the sites were explored by determining whether the concentrations of particulate constituents at one site vary linearly with those at the other. If the correlation between sites is high, and the intercept value is near 0.0 and the slope near 1.0, then we may tentatively conclude that the concentrations at the two sites are effectively identical. If the correlation is high and the slope is 1.0, but the intercept differs from 0.0, we may conclude that there is an excess of the constituent at one site which is not dependent on the abundance at the other. This could be due to the presence of sources local to the site with the excess, or to differences in the particle-size distribu-

TABLE 5. MOREHEAD CITY MEAN PARTICULATE CONCENTRATIONS*

Constituent	Trajectory	Marsh	Roof
Na^+	marine	1.6±1.5	1.7±1.5
	mixed	2.1±1.5	2.5±1.5
	both	1.7±1.4	2.0±1.3
SO_4^{2-}	marine	3.1±2.2	3.7±2.1
	mixed	5.7±1.9	6.6±1.9
	both	4.2±2.1	4.8±2.1
Cl^-	marine	1.6±1.4	1.7±1.5
	mixed	2.1±1.5	2.5±1.5
	both	1.8±1.5	2.0±1.5
Sea salt	marine	3.4±1.5	3.7±1.5
	mixed	3.7±1.6	5.0±1.6
	both	3.5±1.5	4.3±1.6
Excess SO_4^{2-}	marine	2.6±2.3	3.1±2.3
	mixed	5.1±1.9	5.9±1.9
	both	3.7±2.2	3.6±2.6
Excess Cl^-	marine	- 1.4±2.5	- 1.2±2.4
	mixed	- 2.7±1.5	- 1.9±2.5
	both	- 2.0±2.1	- 1.5±2.4
Excess K	marine	0.18±1.52	0.16±1.4
	mixed	0.23±1.6	0.20±2.1
	both	0.19±1.4	0.17±1.7
$EF_{sw}SO_4^{2-}$	marine	7.7 ±1.7	8.7 ±1.9
	mixed	10.8 ±1.6	10.7 ±1.6
	both	9.1 ±1.7	9.6 ±1.7
$EF_{sw}Cl^-$	marine	0.38±3.0	0.47±2.2
	mixed	0.21±2.5	0.37±2.4
	both	0.28±2.9	0.42±2.2
$EF_{sw}K$	marine	4.1 ±1.4	3.5 ±1.3
	mixed	3.9 ±1.4	3.2 ±1.6
	both	4.0 ±1.4	3.4 ±1.4
NO_3^-	marine	0.5 ±1.7	0.8 ±1.3
	mixed	1.9 ±1.9	1.6 ±2.0
	both	1.0 ±2.4	1.1 ±1.9
NH_4^{+**}	marine	0.32±4.5	0.14±1.2
	mixed	0.14±5.6	0.53±4.4
	both	0.23±4.6	0.28±4.2

*Geometric mean ($\mu g\ m^{-3}$) ± 1 geometric standard deviation. Values below the detection limit not used to calculate means.

**NH_4^+ was detectable at the roof only twice on each kind of day.

tions collected at each site, and to the particle-size dependence of the constituents in question. If the correlation is high, and the slope is not equal to 1.0, then we may conclude that the constituent has a source common to both sites, but that there is more at one than at the other, due perhaps to particle-size concentration dependence and distribution effects, or to the fact that one site is closer to a local source than the other.

Table 6 lists the results of the intersite regression analyses performed separately for each class of days. In this table, the roof site is viewed as the dependent variable and the marsh site as the independent variable, so that the equations are for the roof concentration as a function of the marsh concentration.

The roof site is the more exposed of the two, and somewhat closer to the surf zone on the south side of Bogue Banks. In contrast, there are trees and other obstacles around the collector at the marsh, which is at ground level. Therefore, it seems likely that if systematic differences do exist between the correlation of sodium at the two sites, they will be due to a larger proportion of large-particle sodium at the roof.

On "marine" days, the intersite correlation for sodium is extremely high, the intercept of the regression line is near 0.0, and the slope near 1.0. On "mixed" days, the intersite correlation is equally high, but the intercept value indicates that some of the sodium at the marsh is independent of that at the roof. The value of the slope indicates that some of the sodium at the two sites is apparantly of common origin, but the amount at the roof is about 1.36 times that at the marsh. These results on "marine" days therefore seem to imply little difference in particle-size distributions between the two sites, while those on "mixed" days suggest a larger proportion of large-particle sodium at the roof site, and--perhaps--an excess of small-particle sodium at the marsh site.

If this interpretation is valid, then other results listed in Table 6 for "marine" and "mixed" days would seem to imply the following:

1. Excess sulfate occurs chiefly in the small-particle size fraction, and the extremely high correlation between the two sites and the fact that the slope is nearly equal to 1.0 on both classes of days imply

TABLE 6. REGRESSION EQUATIONS BY AIR MASS ORIGIN*

Constituent+		Site	Marine trajectories r	intercept	slope	$\bar{x}_m$	$\bar{x}_r$	Mixed trajectories r	intercept	slope	$\bar{x}_m$	$\bar{x}_r$
A. Intersite Correlations**												
Excess SO_4			0.995	0.41	1.06	3.7	4.3	0.998	0.42	1.00	6.9	7.3
Na			0.98	0.06	1.01	1.7	1.8	0.98	-0.67	1.36	2.4	2.7
Cl loss			0.92	0.15	0.75	1.7	1.4	0.94	-1.34	1.30	2.8	2.3
Excess K			0.94	0.04	0.63	0.20	0.17	0.98	-0.05	1.13	0.27	0.25
NO_3			0.73	0.43	0.68	0.6	0.8	0.96	0.17	1.14	1.5	1.9
NH_4			0.50	--	--	--	--	0.997	0.07	0.90	0.5	0.4
B. Constituent correlations												
Excess SO_4	Cl loss	marsh	0.95	0.15	0.41	3.7	1.7	0.97	1.36	0.24	6.4	2.9
		roof	0.90	0.11	0.30	4.3	1.4	0.92	0.31	0.32	7.3	2.6
Excess SO_4	Excess K	marsh	0.95	0.12	0.02	3.7	0.20	0.98	0.09	0.03	6.4	0.26
		roof	0.98	0.10	0.02	4.3	0.17	0.96	0.03	0.03	7.3	0.25
Cl loss	Excess K	marsh	0.93	0.11	0.05	1.7	0.20	0.93	-0.04	0.10	2.9	0.26
		roof	0.84	0.02	0.09	1.4	0.17	0.92	0.02	0.09	2.7	0.20
Cl loss	NO_3	marsh	0.73	0.37	0.12	1.7	0.6	-0.45	--	--	--	--
		roof	0.56	--	--	--	--	-0.69	--	--	--	--
Excess SO_4	NO_3	marsh	0.83	0.37	0.06	3.7	0.6	-0.61	--	--	--	--
		roof	0.80	0.60	0.05	4.3	0.8	-0.78	2.80	-0.12	7.3	1.9
NH_4	Excess SO_4	marsh	0.96	2.11	10.04	0.16	3.7	0.995	3.61	6.08	0.46	6.4
		roof	0.71	--	--	--	--	0.99	4.6	6.69	0.40	7.3
Na	NO_3	marsh	0.92	-0.06	0.38	1.71	0.60	-0.03	--	--	--	--
		roof	0.70	--	--	--	--	-0.33	--	--	--	--
NH_4	NO_3	marsh	0.81	0.48	0.62	0.16	0.60	-0.58	--	--	--	--
		roof	0.38	--	--	--	--	-0.76	1.76	-0.70	1.92	0.41

* Coefficients are listed only when the correlation is high enough to be significant for normally distributed data.

+ $\bar{x}_m$ and $\bar{x}_r$ are arithmetic means of the marsh and roof values.

**Roof measurements correspond to the dependent variable.

that the concentrations at the two sites are nearly identical, except for a small and consistent excess of about 0.4 μg m^{-3} excess sulfate at the roof. These data are plotted in Figure 7.

2. Chloride loss is greater at the marsh than at the roof on both kinds of days. On "marine" days, this loss does not seem to be due to particle-size differences at the two sites; consequently, it may reflect some active process local to the marsh site. On "mixed" days, there is chloride loss at the marsh which is independent of that at the roof, while the slope of the regression line--which is almost identical to that for sodium on "mixed" days--suggests that the apparently higher chloride loss in constitutents common to the two sites may occur in the large-particle fraction (Figures 8 and 9).

3. There is good correlation between excess potassium at the two sites on both kinds of days, but the regression lines indicate that of the potassium common to the two, there is less at the roof on "marine" days and slightly more on "mixed" days. The results on "mixed" days may reflect a particle-size-related phenomenon, but this does not seem to be the case for "marine" days.

4. The nitrate intersite correlation is modest on "marine" days, when about one-half of the nitrate at the roof is independent of nitrate at the marsh. On "mixed" days the correlation between the sites is high. On these days, of the nitrate common to the two sites, there is slightly more at the roof than at the marsh. On both kinds of days, the slopes of the regression lines for nitrate and excess potassium are similar.

5. Ammonium results show virtually no correlation on "marine" days, and a very high correlation on "mixed" days, when the ammonium at the roof averages about 90% of that at the marsh.

The effects of types of days at the two sites may be further studied by analyzing the interconstituent correlations. Some of these are listed in Table 6.

The most interesting of these results are the high correlations between chloride loss and excess sulfate, which indicate that the loss of the chloride is associated with the presence of gaseous sulfur. In the

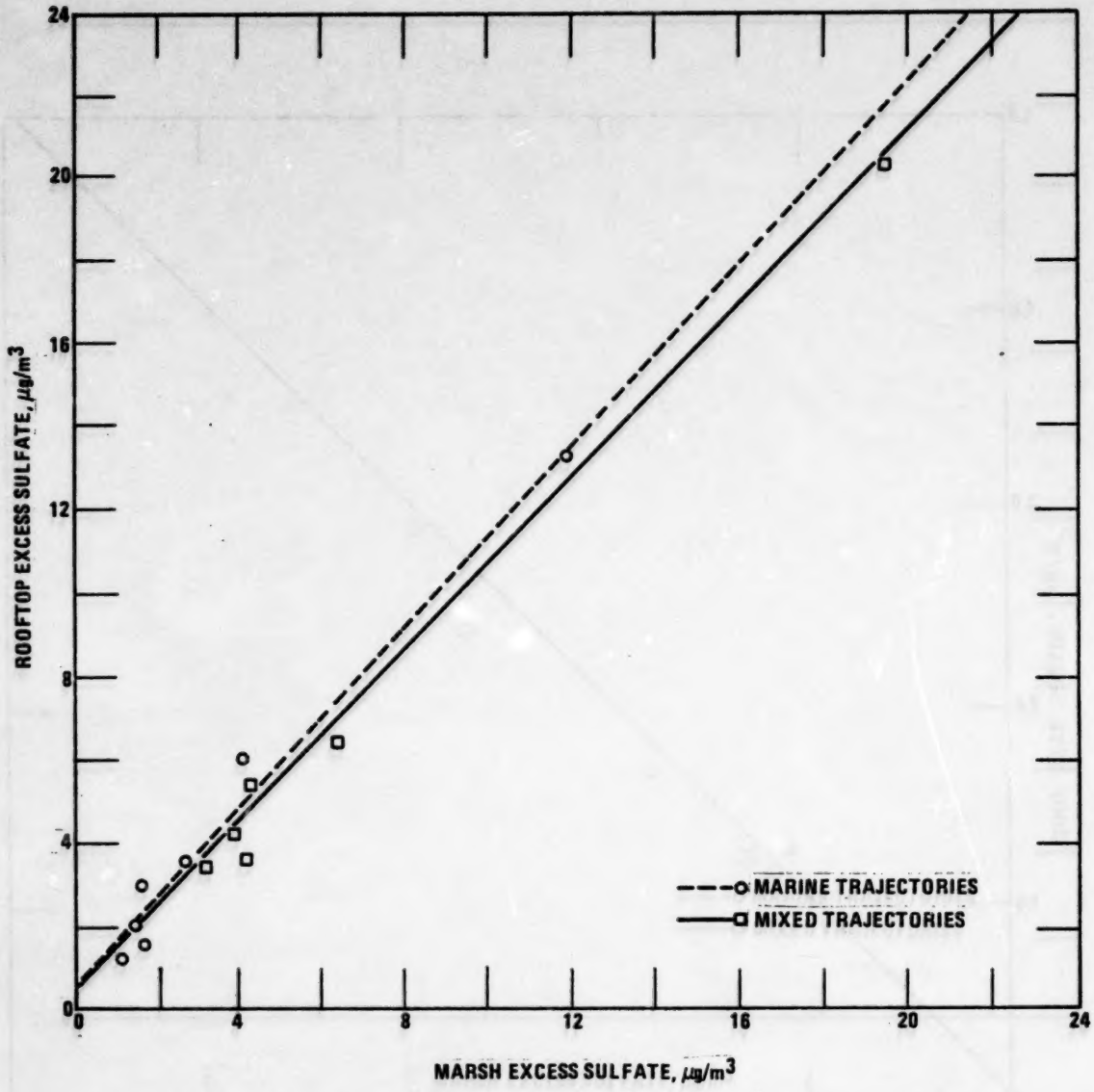

Figure 7. Excess sulfate at Camp Glen roof site and Calico Creek marsh.

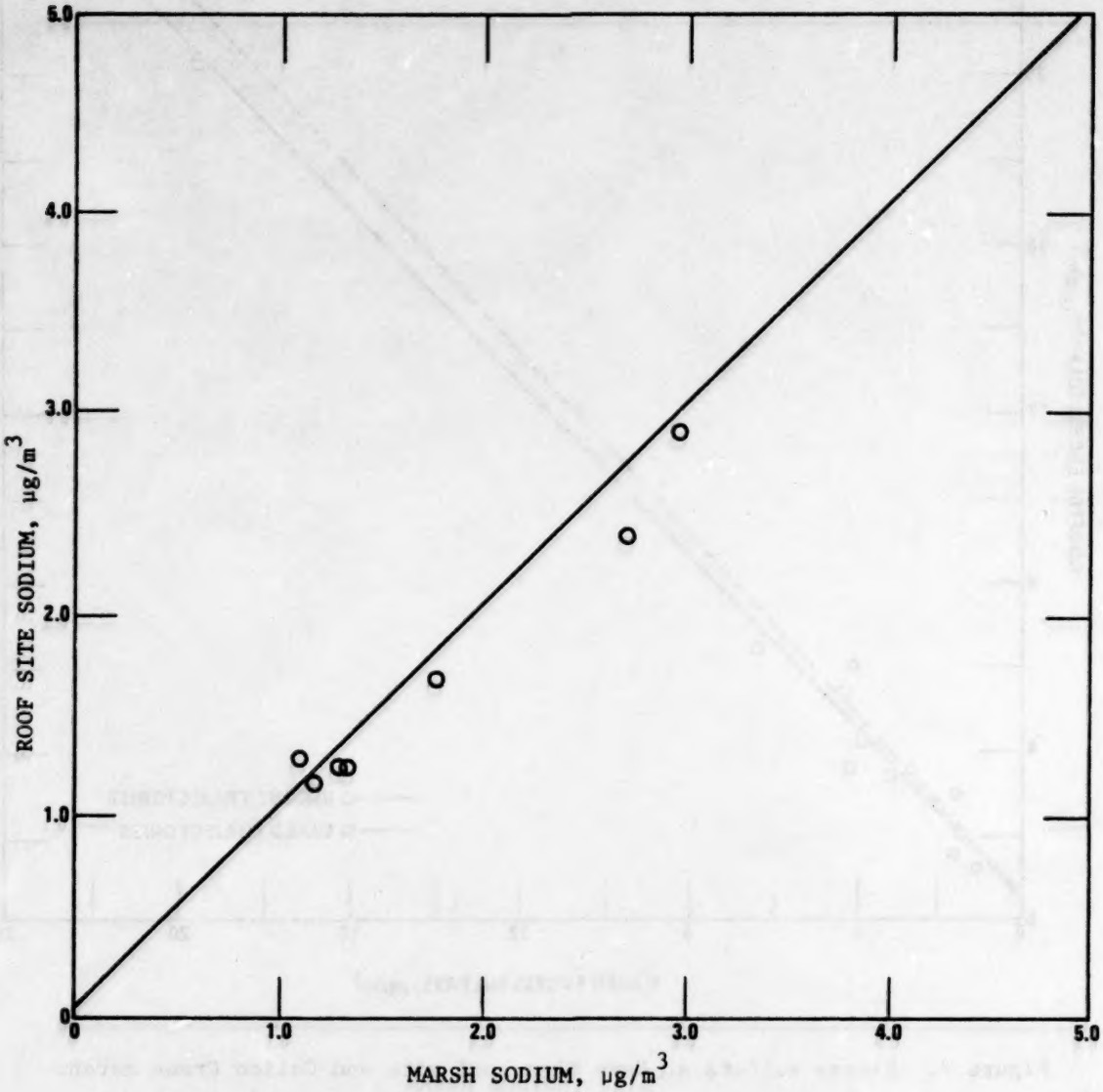

Figure 8. Sodium at Camp Glen roof site and Calico Creek marsh on days with marine trajectories.

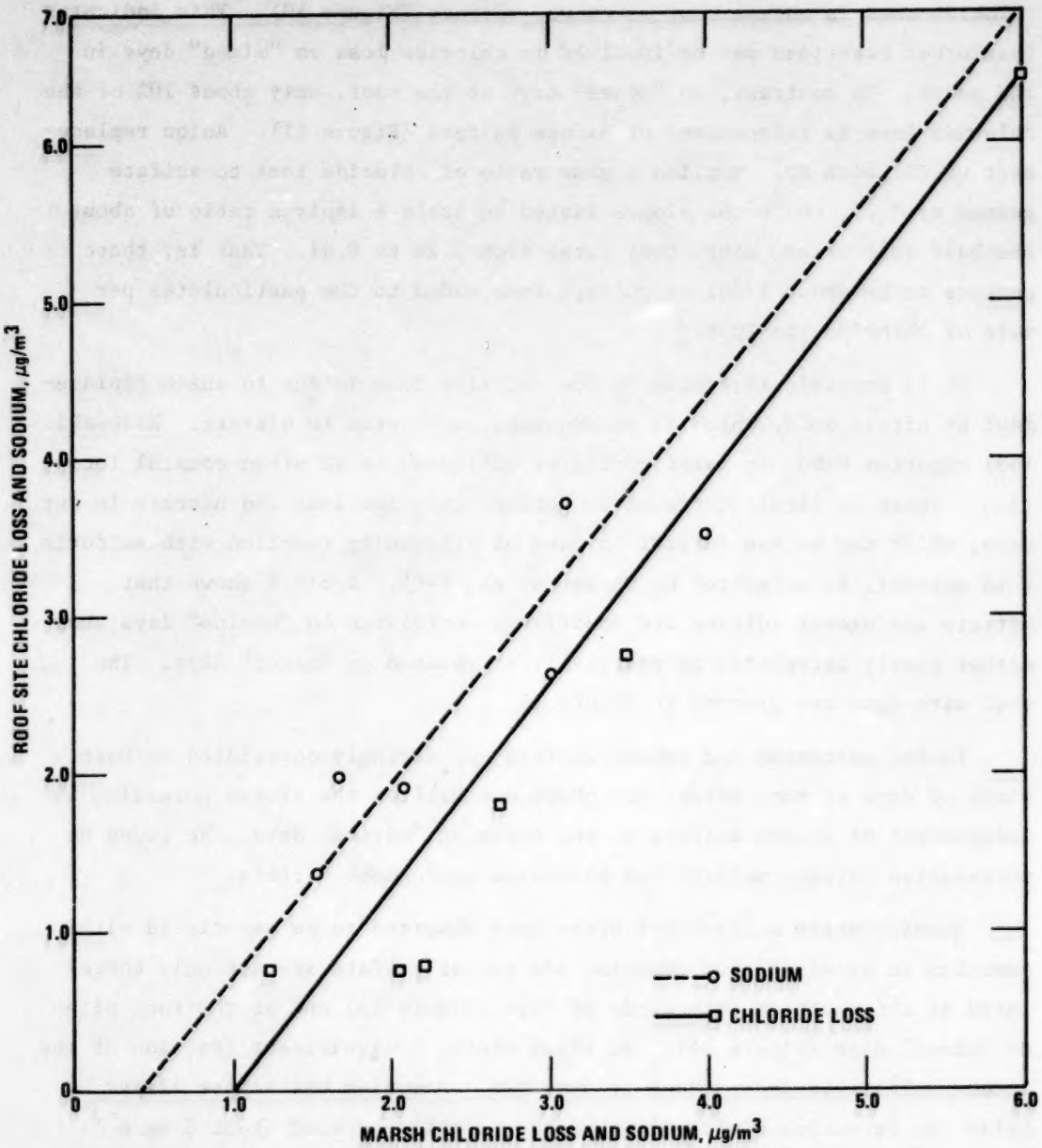

Figure 9. Chloride loss and sodium at Camp Glen roof site and Calico Creek marsh on days with mixed trajectories.

marsh, on "marine" days, most of the chloride loss is associated with excess sulfate, while on "mixed" days, almost one-half of the average chloride loss is independent of excess sulfate (Figure 10). This indicates that other reactions may be involved in chloride loss on "mixed" days in the marsh. In contrast, on "mixed" days at the roof, only about 10% of the chloride loss is independent of excess sulfate (Figure 11). Anion replacement of Cl^- with SO_4^{--} implies a mass ratio of chloride lost to sulfate gained of 0.73, while the slopes listed in Table 6 imply a ratio of about one-half this value, since they range from 0.24 to 0.41. That is, there appears to be about 1 mol of sulfate ions added to the particulates per mole of chloride ion lost.

It is possible that some of the chloride loss is due to anion replacement by nitric acid, which is subsequently converted to nitrate. Kadowaki (45) reported $NaNO_3$ in large particles collected at an urban coastal location. There is little correlation between chloride loss and nitrate in our data, which may be due in part to loss of nitrate by reaction with sulfuric acid aerosol, as suggested by Harker et al. (46). Table 6 shows that nitrate and excess sulfate are positively correlated on "marine" days, but either poorly correlated or negatively correlated on "mixed" days. The roof site data are plotted in Figure 12.

Excess potassium and excess sulfate are strongly correlated on both kinds of days at both sites, but about one-half of the excess potassium is independent of excess sulfate at the marsh on "marine" days. We found no correlation between sulfate and potassium enrichment factors.

Submicrometer sulfate has often been observed to be associated with ammonium in aerosols, and ammonium and excess sulfate are strongly correlated at the marsh on both kinds of days (Figure 13) and at the roof site on "mixed" days (Figure 14). At these times, a significant fraction of the excess sulfate is independent of ammonium. Ammonium was almost always below the detection limit unless excess sulfate exceeded about 3 $\mu g\ m^{-3}$.

Ammonium may also be associated with nitrate, and Kadowaki (45) has demonstrated that small-particle nitrate collected in a coastal urban location consisted of NH_4NO_3. We observed positive correlation between

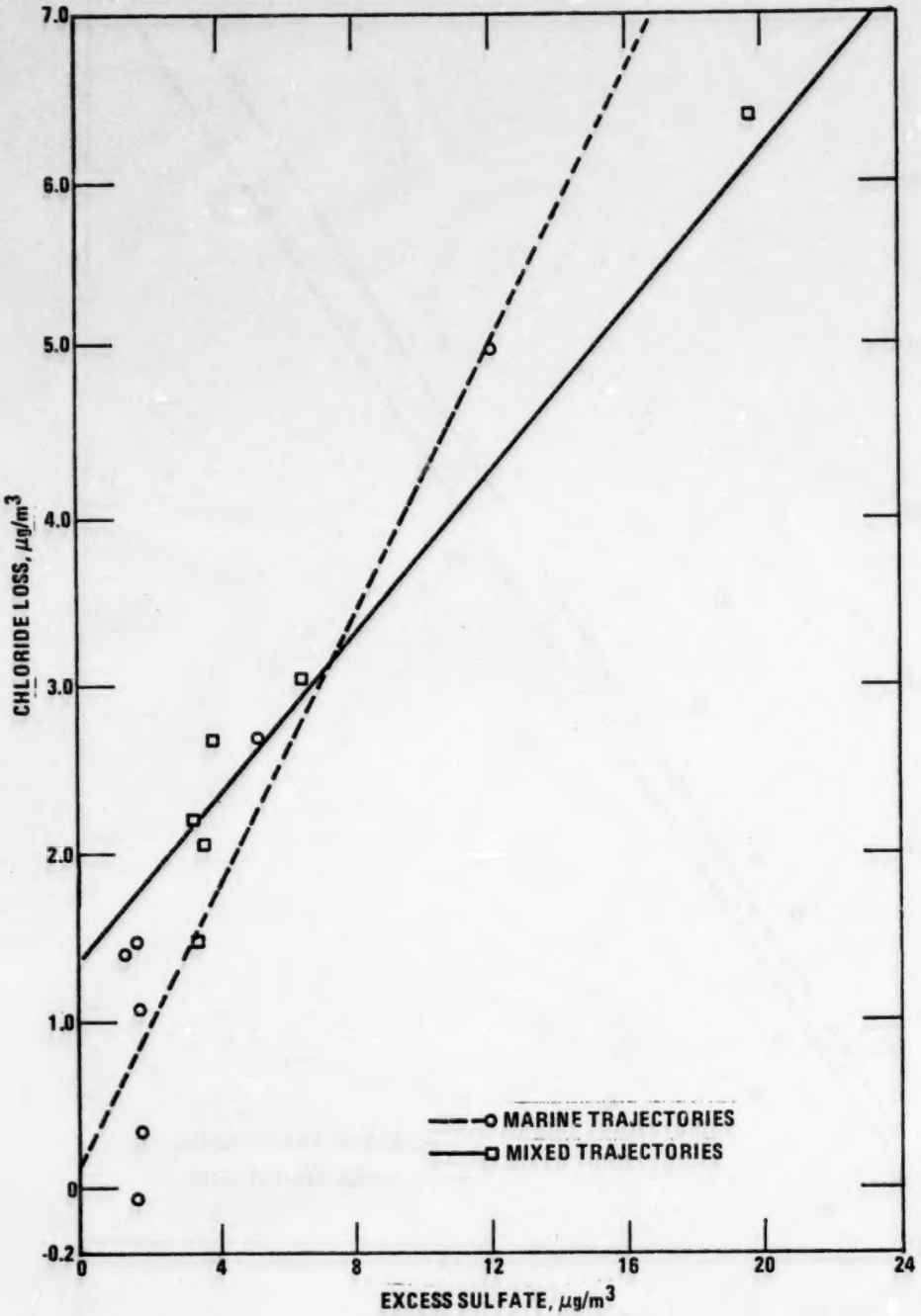

Figure 10. Excess sulfate and chloride loss at Calico Creek marsh.

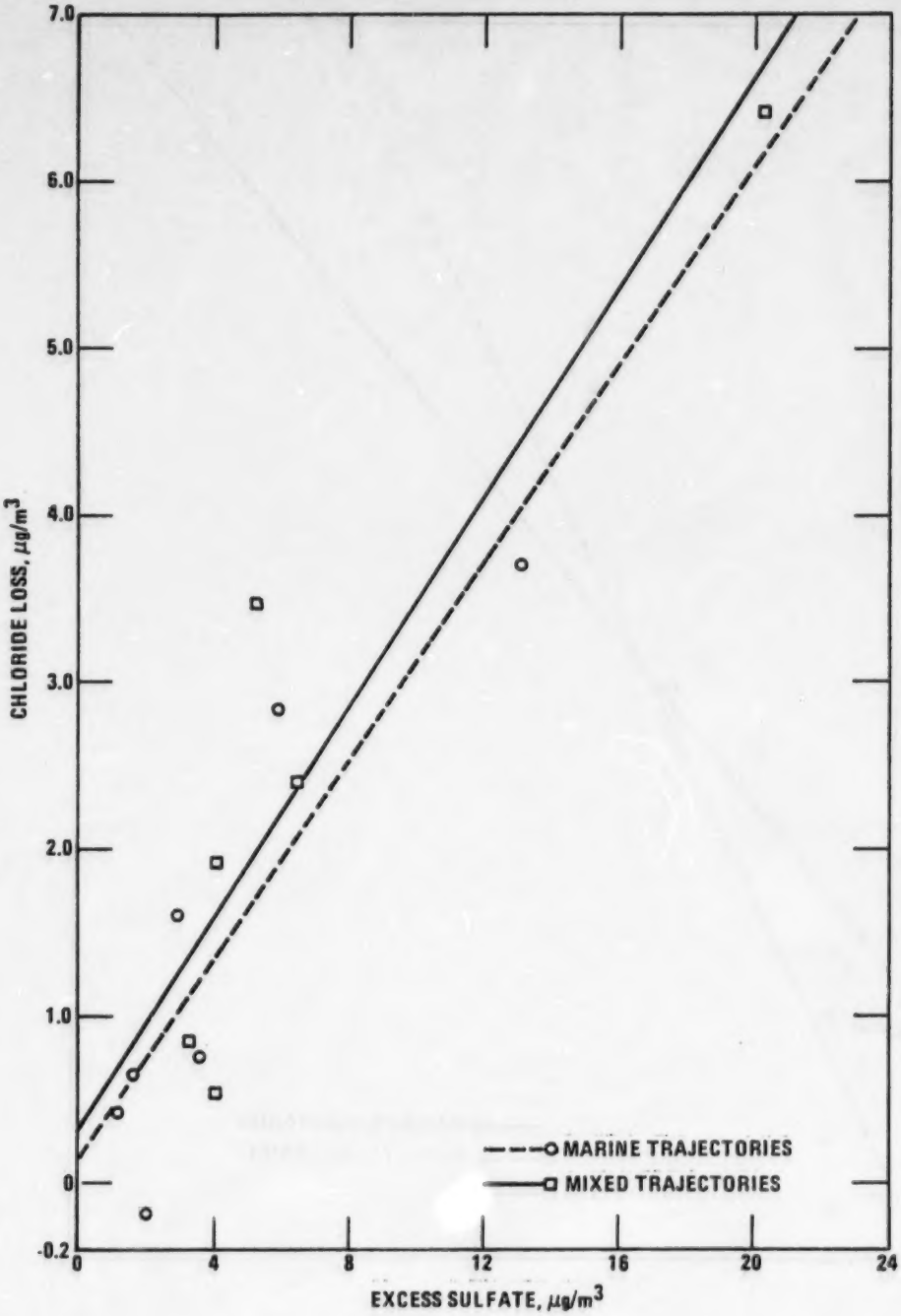

Figure 11. Excess sulfate and chloride loss at Camp Glen roof site.

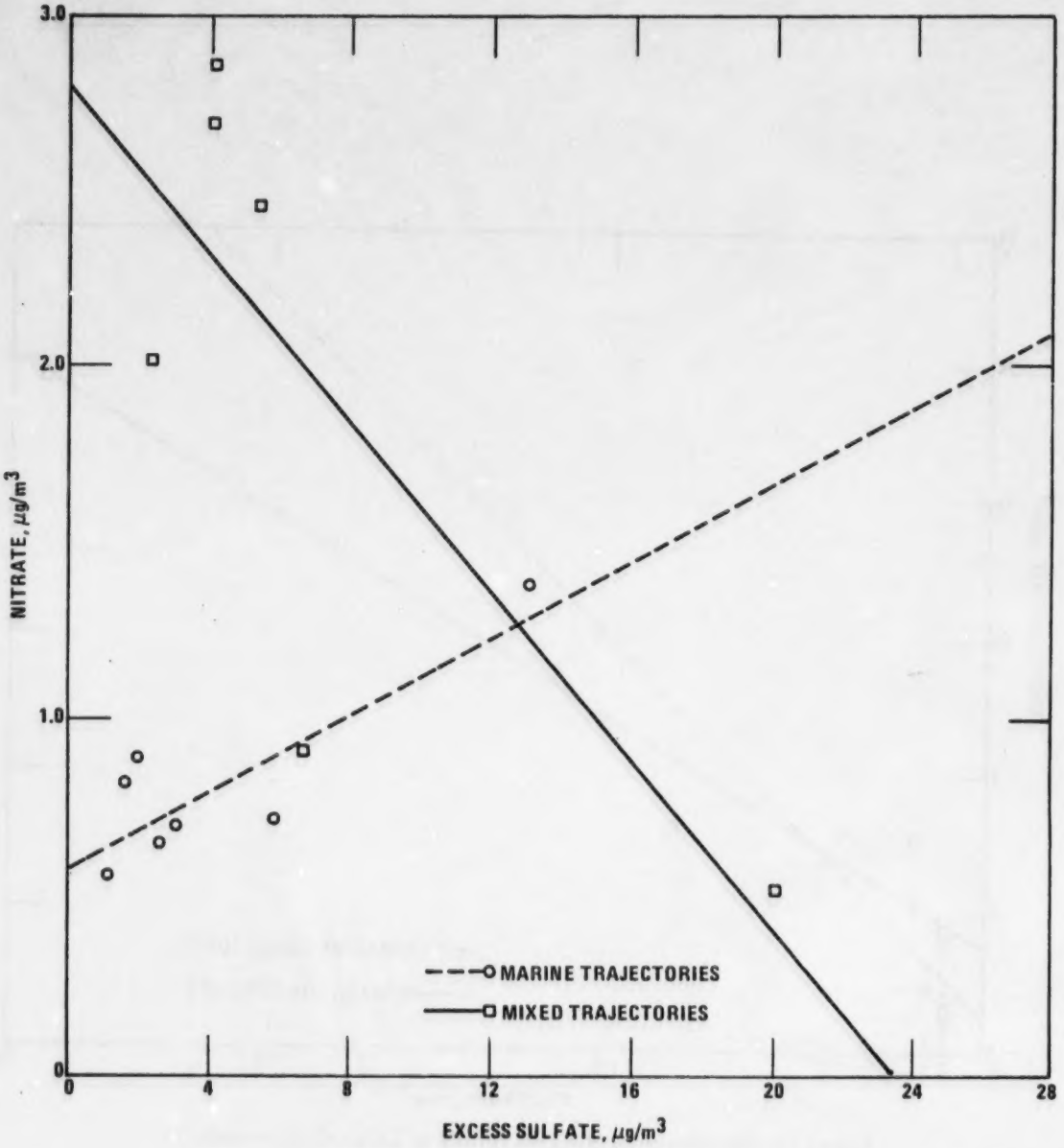

Figure 12. Nitrate and excess sulfate in marine and mixed trajectories at Camp Glen roof site.

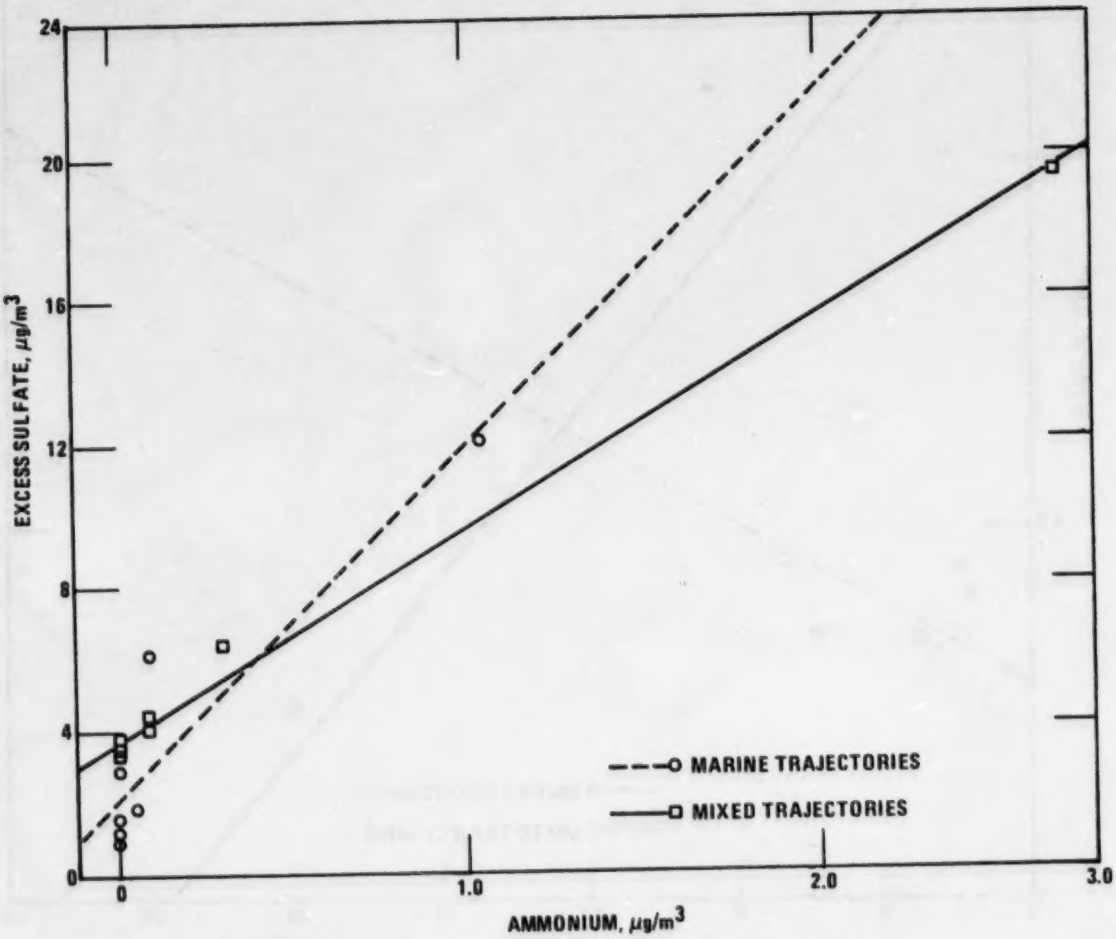

Figure 13. Ammonium and excess sulfate at Calico Creek marsh.

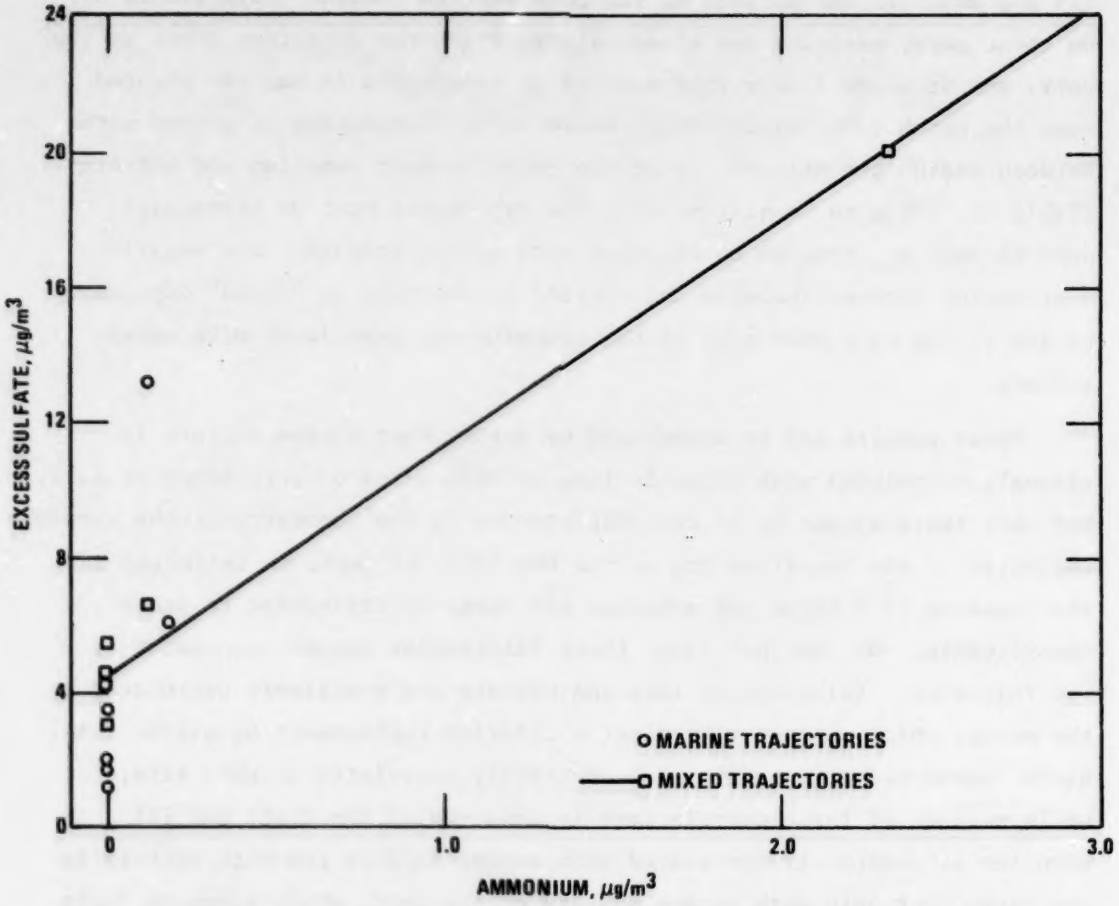

Figure 14. Ammonium and excess sulfate at Camp Glen roof site.

ammonium and nitrate in the marsh on "marine" days, but the intercept value indicates that most of the nitrate is independent of ammonium. Nitrate was also positively correlated with sodium in the marsh on "marine" days, which suggests that both $NaNO_3$ and NH_4NO_3 were present. These results are consistent with those of Kadowaki.

There was only a weak correlation between ammonium and sulfate (Figure 14) and ammonium and nitrate at the roof site on "marine" days (Table 6). On these days, ammonium was almost always below the detection limit at the roof, and it seems likely that most of it originated in sources located near the marsh. On "mixed" days, there is no correlation at either site between sodium and nitrate, or at the marsh between ammonium and nitrate (Table 6). This is consistent with the hypothesis that on these days some nitrate was removed by reaction with excess sulfate. The negative correlation between ammonium and nitrate at the roof on "mixed" days may be due to the fact that most of the ammonium was associated with excess sulfate.

These results may be summarized by saying that excess sulfate is strongly correlated with chloride loss at both sites on both kinds of days, but that there appear to be real differences in the chemistry of the aerosols collected at the two sites and on the two kinds of days, as reflected in the presence of nitrate and ammonium and their relationships to other constituents. On "marine" days, these differences appear to consist of the following: (a) chloride loss and nitrate are positively correlated at the marsh, which appears to reflect a chloride replacement by nitric acid, since sodium and nitrate are also positively correlated at this site, while neither of these correlations is observed at the roof; and (b) ammonium is positively correlated with excess sulfate and with nitrate in the marsh, but only with excess sulfate at the roof, which seems to imply the presence of ammonium nitrate at the marsh, but not at the roof. On "mixed" days, the differences appear to be the following: Excess sulfate is negatively correlated with nitrate at the roof and so is ammonium (correlations at the marsh have the same sign, but are low), which may reflect loss of nitrate by interaction with sulfate that is present together with ammonium.

While there are real differences on "mixed" days between the interconstituent correlations at the two sites, it is not possible to distinguish differences in chemical reactions leading to the formation of aerosols in the two locations from differences in the particle-size distributions in the samples collected at each site.

These conclusions are dependent on the assumption that the particle-size distributions at the two sites are the same on "marine" days, but different on "mixed" days. It is instructive to examine the intersite and interconstituent correlations calculated from all the data, without regard to air mass trajectory classifications. These are shown in Table 7.

Table 7 shows that the intersite correlations continue to be extremely high, but that only K appears to be present in nearly identical concentrations at both sites, as judged from the slope value of 1.02 and the intercept value of -0.03. There appears to be more excess sulfate at the roof site than at the marsh, as revealed by the intercept value of 0.47 $\mu g\ m^{-3}$, but the value of the slope suggests that there is no other systematic difference between the two sites in excess sulfate abundance. The Na relationship shows systematically more sodium at the roof site than at the marsh, but the negative intercept indicates some sodium present at the marsh that is independent of that at the roof. These sodium data may be compared with those for chloride loss, which indicate that chloride loss is greater at the marsh than at the roof site.

The slopes and intercepts of the regression lines for the interconstituent regressions shown in Table 7 are very nearly the same at both sites, except for the correlation between excess sulfate and chloride loss, which indicates that about one-third of the chloride loss observed at the marsh is independent of excess sulfate, while this is the case for only about 10% of the total at the roof site. It will be noted that the slopes of these regression lines imply a loss of about 1.2 mol of chloride ions per mole of sulfate ion gained.

There are no entries in Table 7 for correlations between nitrate and the other constituents, because all of these are very low (<0.30) when the data are grouped. This is to be expected, given that the analyses reported

TABLE 7. REGRESSION EQUATIONS - ALL DAYS*

Constituent[+]			r	intercept	slope	$\bar{x}_m$	$\bar{x}_r$
A. Intersite Correlations[++]							
Excess SO_4			0.997	0.47	1.01	5.2	5.7
Na			0.98	-0.24	1.19	2.1	2.2
Excess Cl			0.91	-0.30	0.97	2.2	1.8
Excess K			0.96	-0.03	1.02	0.24	0.21
NO_3			0.96	0.20	1.11	1.02	1.33
NH_4			0.95	-0.06	0.80	0.36	0.23
B. Constituent Correlations							
Excess SO_4	Cl loss	marsh	0.93	0.75	0.31	5.1	2.3
		roof	0.92	0.16	0.32	5.7	2.0
Excess SO_4	Excess K	marsh	0.97	0.10	0.03	5.1	0.23
		roof	0.93	0.06	0.03	5.7	0.21
Cl loss	Excess K	marsh	0.88	0.07	0.07	2.3	0.23
		roof	0.88	0.07	0.07	2.0	0.21
NH_4	Excess SO_4	marsh	0.96	3.0	6.69	0.31	5.1
		roof	0.85	4.2	7.04	0.21	5.7

*Coefficients are listed only when the correlation is high enough to be significant for normally distributed data.

[+] $\bar{x}_m$ and $\bar{x}_r$ are arithmetic means of the marsh and roof values.

[++] Roof measurements correspond to the dependent variable.

above showed that these are strongly dependent on air mass trajectory classification. These results would appear to validate the air mass trajectory classifications.

PARTICULATE ABUNDANCES AT SWANSBORO

Only five samples were collected at each site, due to adverse weather conditions and other problems. The resulting concentration data were analyzed in a manner similar to that employed for the Morehead City data, except that the small number of data points precluded use of the Sign Test. Trajectory analyses indicated that air masses with wholly continental trajectories were sampled on all days, although local surface winds often blew from the Atlantic Ocean, and windspeeds up to 10 to 15 m s^{-1} occurred some of the time.

As might be expected under these conditions, sea salt was present in all samples, the more exposed site at the Coast Guard Station showing systematically higher concentrations and a larger range--2.5 to 40 μg m^{-3}--as opposed to the other two sites, where sea salt ranged from 2.2 to 7.0 μg m^{-3}.

Geometric means of constituents of interest are shown in Table 8. Statistical comparisons showed that both total chloride and total sodium at the Coast Guard Station significantly exceeded that at Little Kinston ($p_{H_0} < 0.05$ as determined by Student's t-test of the significance of the difference between the mean logs). The mean levels of these constituents at Breezy Point were slightly higher than those at Little Kinston, and differences between this site and those at the Coast Guard Station were only marginally significant ($p_{H_0} < 0.1$).

All samples contained excess sulfate and exhibited evidence of chloride loss. At the Coast Guard Station chloride loss ranged from 1.9 to 7.0 μg m^{-3}, and chloride enrichment from 0.05 to 0.92. Excess sulfate at this site ranged from 2.3 to 6.6 μg m^{-3}, and sulfate enrichment factors from 5 to 16.3. At the other two sites in more protected locations, chloride loss ranged from 2.8 to 5.8 μg m^{-3}, and sulfate enrichment factors ranged from 12.6 to 33.3.

TABLE 8. SWANSBORO MEAN PARTICULATE CONCENTRATIONS*

Constituent	Coast Guard Station	Breezy Point	Little Kinston
Na^{+} +	6.2 ± 2.2	2.7 ± 1.3	2.3 ± 1.3
SO_4^{2-}	5.3 ± 1.5	4.5 ± 1.4	4.1 ± 1.4
Cl^{-} +	4.6 ± 2.0	0.7 ± 2.9	0.4 ± 2.5
Sea salt^{+}	10.5 ± 3.7	4.3 ± 1.5	3.3 ± 1.4
Excess SO_4^{2-}	3.4 ± 1.6	3.8 ± 1.5	3.2 ± 1.4
Excess Cl	-3.7 ± 1.6	-4.0 ± 1.3	-3.6 ± 1.2
Excess K	0.66 ± 1.48	0.62 ± 1.36	0.55 ± 1.52
$EF_{sw}SO_4^{2-}$	4.4 ± 1.4	6.6 ± 1.5	6.6 ± 1.3
$EF_{sw}Cl^{-}$	0.4 ± 3.3	0.1 ± 2.3	0.1 ± 1.9
$EF_{sw}K$	3.8 ± 1.4	6.4 ± 1.5	6.2 ± 1.3
NO_3^{-} ++	1.00 ± 3.02	0.06 ± 3.43	0.13 ± 3.55
NH_4^{+}	0.57 ± 1.31	0.61 ± 1.86	0.57 ± 1.87

* Geometric mean and geometric standard deviation. Values below detection limit were not used in calculating the means. Units are $\mu g\ m^{-3}$ except for enrichment factors, which are dimensionless.

+ Differences between Coast Guard Station and Little Kinston means are significant beyond the 0.05 level. Differences between Coast Guard Station and Breezy Point means are marginally significant.

++ Differences between Coast Guard Station and Breezy Point means are significant beyond the 0.05 level. Differences between Coast Guard Station and Little Kinston means are marginally significant.

Ammonium was observed in all samples and ranged from 0.3 to 1.1 $\mu g\ m^{-3}$, while nitrate was observed in all but four samples, and ranged up to 3.1 $\mu g\ m^{-3}$. Potassium was present in all samples, and ranged from 0.4 to 1.5 $\mu g\ m^{-3}$.

The most striking feature of these data was the chloride depletion exhibited in all samples. It ranged from 7 to 95% at the Coast Guard Station, 59 to 96% at Breezy Point, and from 77 to 96% at Little Kinston. The mean losses were 40% at the Coast Guard Station and 90% at the other two sites. The air masses sampled were always continental and had spent effectively no time over the ocean, and there are no significant nonmarine sodium sources in this region. We therefore infer that the reactions leading to the chloride depletion were rapid ones.

Analyses of the dependence of the concentrations of constituents at each site on their concentrations at the others showed high intersite correlations for excess sulfate, sodium, and excess potassium, but moderate or low correlations for ammonium, nitrate, and chloride loss. In general, the two protected sites tended to exhibit stronger intersite correlations than either did with the Coast Guard Station. None of the sodium regression lines implied similar particle-size distributions at any pair of sites.

Chloride loss shows no correlation with excess sulfate, potassium, nitrate, or ammonium at any site. Ammonium was correlated with excess sulfate at all sites, but the correlation was higher at the two protected sites ($r = 0.92$ and 0.98) than at the Coast Guard Station ($r = 0.78$).

The wide range of sodium and sea salt concentrations at the Coast Guard Station implies that the samples collected here on different days differed in the proportion of large-particle sea salt aerosols present. If this is the case, then there should be a negative correlation between sodium and enrichment factors of constituents which are present chiefly in the small particle fraction, and a positive correlation between sodium and chloride enrichment. These were observed. The correlation between sodium and sulfate enrichment factor was -0.999, that between sodium and potassium was -0.95, and that between sodium and chloride enrichment was 0.86. These results imply that correlations between enrichment factors in

non-size-segregated particulate samples do not necessarily imply common sources for the corresponding elements or ions, since this may be an artifact of particle-size dependence, combined with variations in particle-size distributions in the samples in question. Excess sulfate was observed to correlate well with excess potassium at all sites ($r = 0.80$ to 0.98). Since their enrichment factors were not correlated with sodium at Breezy Point or Little Kinston, we infer that the association between the two constituents was probably real.

We may summarize these results by saying that excess sulfate is present in all samples, but there is no evidence other than its correlation with excess potassium to suggest that it is of biogenic origin. Chloride loss is also observed in all samples but showed no systematic relationship to any other constituent consequently, no simple anion-replacement process is implied. The coastal location of the sites and the fact that all air masses had traversed the continent before reaching the sampling location implies that chloride loss is a rapid process in coastal locations.

SECTION 6

DISCUSSION

HYDROGEN SULFIDE AND SULFUR DIOXIDE

The observation of H_2S in the atmosphere at levels above 1.4 $\mu g/m^3$ (1 ppb) in both Morehead City and Swansboro, and of SO_2 at Swansboro at levels up to 45 $\mu g/m^3$ (17 ppb) during high winds implies that these are biogenic and that they must be derived from the metabolism of bacterial sulfate reducers, and not from the decomposition processes described by Challenger (53), and Kadota and Ishida (8), and proposed by Lovelock et al. (9) as the source of 100 million tons of atmospheric sulfur per year. This is implied by the high levels observed, by the association between tidal mud exposure and H_2S concentration in the atmosphere at the marsh site, and by the absence of anthropogenic sources of SO_2 or H_2S at Swansboro.

The observation of variable and sometimes very high concentrations of H_2S associated with the exposure of mud in Calico Creek is consistent with the observations of Hansen et al. (33) and Brannon (30), who observed large H_2S emissions from tidal pools and exposed tidal muds. They also confirm the commonplace observation that H_2S can be detected by its odor near tidal marshes and other sites where it is produced by bacterial sulfate reducers.

The higher low-tide H_2S concentrations observed at night in the marsh may be due to the lower windspeeds experienced then. However, the failure of low-tide daytime H_2S concentrations to exhibit any systematic relationships to surface windspeed suggests that other factors may be at work. There are several candidates.

The daytime H_2S concentrations may reflect atmospheric dispersion effects that depend on vertical turbulence and mixing heights as well as on horizontal windspeeds, effects that are probably more important in the

daytime that at night. It is also possible that the H_2S emissions differed systematically due to differences in the area and duration of mud exposure during low tides during the day as compared to low tides at night.

Furthermore, several purely biological processes are known to reduce the daytime concentrations of H_2S in the interstitial water of organic-rich muds like those at the Calico Creek site. Chief among these are the activity of the green and purple photosynthetic sulfur bacteria which oxidize H_2S in the daytime, and the daytime release of photosynthetically produced O_2 from the roots of Spartina plants. Jørgensen and Fenchel (21), Jørgensen (22), Hansen et al. (33), and Brannon (30) have all documented the influence of one or both of these factors on H_2S abundance in interstitial muds. Green and purple sulfur bacteria could be observed in the surface muds of Calico Creek, and it is likely that their presence and that of the S. alterniflora acted to lower the H_2S emissions during the daytime.

The nearly total absence of H_2S at the roof site on occasions when it was abundant in the marsh is interesting. It suggests that either the total H_2S emissions from the marsh were quite low, or that H_2S was rapidly removed from the atmosphere after it was evolved from the surface muds. Since we have no basis for estimating the flux of H_2S from the marsh, we cannot choose between these alternative explanations. The area of the marsh is only about 0.5 km^2; consequently, it represents only about 3% of the land area of a circle with the marsh sampling site at its center and the roof site on its perimeter. It should also be noted that if the failure to observe H_2S at the roof site is due in part to its rapid removal from the atmosphere, then this removal occurs at night as well as during the daytime, and the H_2S does not appear to be converted to SO_2.

The results of the estuarine experiment contrast sharply with those of the marsh experiment. At this time we observed widespread occurrence of H_2S independent of the local tidal cycle and also observed considerable SO_2. The correlation of H_2S and SO_2 detected at the Coast Guard Station indicates that both have a common source and this fact, together with the absence of significant local anthropogenic SO_2 and H_2S sources, implies that both are derived from biological processes and that the SO_2 was produced from the H_2S. The correlation between H_2S at the other two sites

suggests either that the H_2S is derived from a single common source in these locations, or that it is released in synchrony from sources local to both Breezy Point and Little Kinston.

The origin of this H_2S remains obscure. We have pointed out above that while many authors have claimed that H_2S cannot be evolved from surface water because it is too rapidly oxidized by O_2 in water, the available evidence indicates that under some conditions H_2S may be quite stable in natural waters. This suggests that the H_2S we observed may have been derived from anoxic underwater sediments and may have evolved into the atmosphere from the surface of the water. The high windspeeds and swift currents could have promoted this release.

Alternatively, it is possible that biogenic H_2S may be released to the atmosphere from anoxic levels in coarse sand that have been observed 10 to 50 cm below the surface (54). If so, then the exposed sand bars near the Coast Guard Station and the shore sediments near all three sites could have contributed to the observed H_2S levels. In any case, it seems likely that the SO_2 was derived by atmospheric oxidation from H_2S, which implies that the half-life of H_2S in this environment may be on the order of minutes, rather than hours, as proposed by Sprung (55).

The contrast in the results obtained at Morehead City in the summer and at Swansboro later in the year is puzzling. If both H_2S and SO_2 can be derived from coarse sand sediments and/or surface water in the fall at Swansboro, why were these two not observed at the roof site the previous summer, since these kinds of sources exist near that site? It seems likely that the differences are due to the difference in the season, either seasonal variations in the biological or physical processes responsible for the release of these gases from such sites (which seems unlikely), or in the processes that govern their atmospheric fate.

PARTICULATE SULFATE AND OTHER CONSTITUENTS

As we have pointed out above, the particulate results obtained at Morehead City are somewhat ambiguous, in that the interconstituent regressions for excess sulfate, chloride loss, and excess potassium do not differ greatly between sites if all samples are analyzed together. These results

show that chloride loss is greater at the marsh than at the roof site, and that some of the chloride loss at the marsh is independent of that at the roof.

If we separate the observations by air mass trajectory classification, the differences between the sites become more pronounced. High inter-constituent correlations between some other constituents are observed on some classes of days. These results involve the abundance and intersite correlations of ammonium and nitrate, and their relationships to excess sulfate and sodium. Since these results are compatible with the observations of other workers, we are inclined to think that they validate the air mass trajectory classifications.

The presence of excess sulfate on "marine" days indicates that it is probably biogenic in origin. The fact that excess sulfate is strongly associated with excess potassium but not with iron or vanadium on both kinds of days, and that the relationship between chloride loss and excess sulfate is similar on both "marine" and "mixed" days suggests that much of the particulate sulfate present on "mixed" days is also biogenic.

The high correlation between chloride loss and excess sulfate observed at both Morehead City sites indicates that most of the chloride loss was due to replacement by sulfate anions, at a ratio of approximately one chloride ion lost per excess sulfate ion gained. The evidence indicates that ammonium sulfate and ammonium nitrate are present in the fine particle fraction at the marsh on "marine" days, and that some of the chloride loss may be due to anion replacement by nitric acid, as proposed by Robbins et al. (41) and observed by Martens et al. (37), and Kadowaki (45). However, the failure to observe strong positive correlation between nitrate and chloride loss on "mixed" days (which would be expected if NaCl were replaced by $NaNO_3$) may be due to loss of some of the nitrate by reaction with sulfuric acid aerosols (or even SO_2) as proposed by Harker et al. (46). This appears likely in view of the slight negative correlation between excess sulfate and nitrate on "mixed" days at the roof site, which contrasts sharply with the positive correlation between these constituents at both sites on "marine" days.

The particulate results observed later in the year at Swansboro are not comparable to those observed at Morehead City, due to the difference in season and the fact that all air masses sampled had passed over the continent and none had spent time over the ocean. The fact that chloride loss was observed in all these samples is interesting, since it suggests that chloride loss due to interaction with atmospheric S (as SO_2, H_2SO_4, or some other species) occurs rapidly.

The evidence available from Swansboro provides very little insight into the question of the possible biogenic origin of the excess sulfate, other than its association with excess K.

Hoffman and Duce (56) showed that potassium is not enriched relative to sodium in aerosols collected in Hawaii from the trade winds under conditions that carefully eliminate contaminated air from land sources. Hoffman et al. (57) showed that potassium enrichment in marine aerosols collected from shipboard in the Atlantic Ocean is very low (e.g., 1.05 or less) if little iron or dust of continental origin is present, but may otherwise be large. Their work implies that potassium enrichment is due largely to contamination from land sources. However, Chesselet et al. (39) demonstrate that small-particle potassium may be derived from the organic film at the surface of the ocean, and they report its presence in the Mediterranean Sea and in the Atlantic Ocean. Buat-Menard et al. (35) observed potassium enrichment near the Gulf of Guinea in aerosols that did not contain insoluble dusts, calcium, or other evidence of dusts derived from continental sources, and inferred that both excess sulfate and potassium were derived from the ocean surface in this biologically productive region. The simultaneous observation of chloride loss balanced by excess sulfate indicated to these authors that the chloride loss was due to anion replacement by sulfuric acid derived from biogenic gaseous sulfur originating in the productive surface waters.

The fact that excess sulfate, chloride loss, and excess potassium are highly correlated at Morehead City, while none of these are correlated with iron, lead, or vanadium, suggests that the sulfate is biogenic. However, it seems that a negative correlation between sulfate and chloride enrichment

factors does not always imply a causal relationship but may reflect day-to-day variations in the large-particle sodium abundance, as occurred at the Swansboro Coast Guard Station.

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